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## AN INVESTIGATION ON WETTING OF POROUS MATERIALS

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Indirect methods of evaluation of wetting properties of fine particles or porous materials require selection of a reference liquid, for which the contact angle is equal to zero. In our investigation, the capillary rise method and film flotation were used for: glass microglobules - water and glass microglobules – decane systems. The data for the reference liquid and the examined one are introduced into the modified Washburn equation and the contact angle is calculated.

*key words: capillary rise, film flotation, porous materials, wetting, contact angle*

### INTRODUCTION

There are several simple and fast methods to determine contact angle on a flat surface, e.g. sessile drop (captive bubble), inclined plate, and Wilhelmy's plate methods. However, determination of the contact angle on porous materials is more challenging. Intermediate methods are required to evaluate wetting properties of porous or loose materials. The methods include: the capillary rise, "wick", compressed disc, film flotation and recently the atomic force microscopy (Xu and Masliyah, 2002). In our paper the capillary rise method was combined with the film flotation method. Such approach to finding the reference liquid is proposed for the first time.

### CAPILLARY RISE METHOD

The capillary rise method is based on measurements of capillary pressure difference or velocity of liquid penetration through a porous material. Bartell et al. (1932, 1934) were first to employ this method in research. The quantity they measured was

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the value of pressure applied to the system, while the quantity determined was the pressure required to stop the liquid from penetrating further into the bed. When the velocity of penetration is equal to zero the system is in equilibrium described by the formula:

$$\Delta P = \frac{2\gamma \cdot \cos \theta}{r} \quad (1)$$

where  $r$  is the average diameter of capillaries in the porous material.

The apparatus for measuring capillary pressure is shown on Fig. 1.

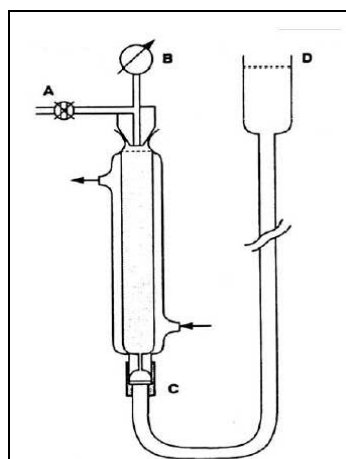


Fig. 1. Capillary pressure measuring apparatus: A - control valve, B - pressure converter, C -capillary pipe, D - liquid container (Diggins et al., 1990).

The velocity of penetration is measured in a column with a filler. The method is based on the assumption introduced by Washburn (1921) that the porous system comprises of  $n$ -cylindrical capillary pipes.

Levine et al., (1980) and Xue (2006) assumed that porous materials behave like a bundle of capillaries and a modified Lucas-Washburn (Hamraoui and Nylander, 2002; Xue et al., 2006) equation is used:

$$h^2 = \frac{(c\bar{r})\gamma_{LV} \cdot \cos \theta \cdot t}{2\eta} \quad (2)$$

where  $c$  is a constant.

After reforming previous equation we obtain:

$$r = \frac{6\eta\gamma_{LV} \cos\theta \cdot h^2}{-2\rho g\eta h^3 + 3\gamma_{LV}^2 \cos^2\theta \cdot t}. \quad (3)$$

In the last equation  $\theta$  is the only unknown parameter.

The capillary rise method is based on the Washburn equation that has been derived from Poiseuille equation:

$$dV = \frac{r^4 \cdot \Delta P \cdot \pi}{8\eta \cdot h} dt. \quad (4)$$

Thus, the Washburn equation is (Washburn 1921):

$$h^2 = \frac{r \cdot \gamma \cdot \cos\theta}{2\eta} t. \quad (5)$$

Additionally, the following simplifications are employed in the capillary rise method:

- the flow is laminar and stationary
- there is no slip, i.e. no flow on the solid body - liquid interface
- no internal pressure.

It is more convenient to use the modified Washburn equation which represents the dependence of change in liquid mass on time (Siebold, 1997, Diggins, 1990)

$$m^2 = \frac{C \cdot \rho \cdot \gamma \cdot \cos\theta}{\eta} \cdot t \quad (6)$$

where constant  $C$  is:

$$C = \frac{r(\pi R_k^2)^2 \varepsilon^2}{2} \quad (7)$$

and where:

$h$ – height of penetration	$\varepsilon$ – bed porosity
$r$ – average capillary pipe diameter	$\rho$ – penetrating liquid density
$\gamma$ – penetrating liquid surface tension	$t$ – time of penetration
$\eta$ – penetrating liquid viscosity	$m$ – penetrating liquid mass increase
$\theta$ – contact angle	$R_k$ – glass tube inner diameter.

One way to determinate contact angle are investigations involving two liquids – the reference and examined (Studebaker, 1955) ones. For the reference liquid:

$$h^2 = \frac{r\gamma_0}{2\eta_0} t_0. \quad (8)$$

For identical beds  $r$  is constant, therefore, for the liquid being examined we have:

$$h^2 = \frac{r\gamma_1 \cos \theta}{2\eta_1} t_1. \quad (9)$$

Dividing equations (8) and (9) we obtain

$$\cos \theta = K \frac{t_0}{t_1} \quad (10)$$

where

$$K = \frac{\gamma_0 \cdot \eta_1}{\gamma_1 \cdot \eta_0} \quad (11)$$

and where

$t_0, \gamma_0, \eta_0 \rightarrow$  time of penetration, surface tension and viscosity of reference liquid  
 $t_1, \gamma_1, \eta_1 \rightarrow$  time of penetration, surface tension and viscosity of liquid investigated.

Another way to determine contact angle is to calculate the mean capillary radius (assuming that the glass microglobules behave like a bundle of capillaries) using Eq. (3) and then calculating the contact angle using the Washburn equation (Eq. 15).

#### FILM FLOTATION METHOD

The method of film flotation is used to determine the contact angle of fine particles. The behavior of a small particle in contact with surface of a liquid depends mainly on surface tension of the given liquid. The following states of the particle are distinguished: State I occurs when the particle is dropped toward the surface of the liquid but is still in the gas phase. State II occurs when the particle contacts the surface of the liquid. Next, depending on the contact angle of the substance either State III (the formation of a three-phase wetting line) or State IV (the particle stays just below the surface of the liquid - it is fully immersed) is obtained or the particle sinks (Fig. 2) (Bartell and Walton, 1932; Churaev, 2005; Feurstenau et al., 1991).

The total sum of energy (transition from State I to State IV) is the sum of kinetic, potential and interfacial energies:

$$\Delta G_r = \Delta G_K + \Delta G_P + \Delta G_I \quad (12)$$

The change in interfacial energy is, in turn, the sum of changes in adhesion, spill and immersion energies:

$$\Delta G_I = \Delta G_a + \Delta G_l + \Delta G_s \quad (13)$$

$$\Delta G_a = -\gamma_{SV} + \gamma_{SL} - \gamma_{LV} \quad \text{adhesion work} \quad (14)$$

$$\Delta G_i = -\gamma_{SV} + \gamma_{SL} \quad \text{immersion work} \quad (15)$$

$$\Delta G_s = -\gamma_{SV} + \gamma_{SL} + \gamma_{LV} \quad \text{spill work} \quad (16)$$

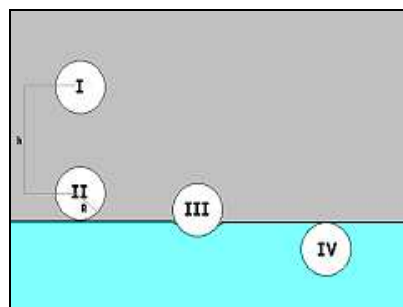


Fig. 2. Behavior of particles on a liquid surface

Employing the Young equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (17)$$

one obtains:

$$\Delta G_a = -\gamma_{LV} (\cos \theta + 1) \quad (18)$$

$$\Delta G_i = -\gamma_{LV} \cos \theta \quad (19)$$

$$\Delta G_s = \gamma_{LV} (\cos \theta - 1). \quad (20)$$

When  $\theta < 180^\circ$  the adhesional wetting will be spontaneous, when  $\theta < 90^\circ$  immersion wetting will be spontaneous and when  $\theta = 0^\circ$  spill wetting will be spontaneous.

## EXPERIMENTAL PART

Glass microglobules of real density  $2410 \text{ kg/m}^3$  (apparent density  $1773 \text{ kg/m}^3$ ) and diameter  $150 - 250 \mu\text{m}$  (see Fig. 3) were used. The oxide composition is as follows:

$\text{SiO}_2$	70 – 73%
$\text{Na}_2\text{O}$	13 – 15%
$\text{CaO}$	7 – 11%
$\text{Fe}_2\text{O}_3$	max 0,1%.

Before the experiment, microglobules were thoroughly cleaned and degreased, first by immersion in a mixture of solvents comprising of methanol : acetone : chloroform (1:1:1 by volume) and subsequently, washed with chloroform, methanol, acetone and water. Finally, they were dried at  $130^\circ\text{C}$  for a constant weight. Glass capillaries



were filled with predetermined amount of beads and placed in a shaker in order to provide uniform packing of glass spheres in the bed.

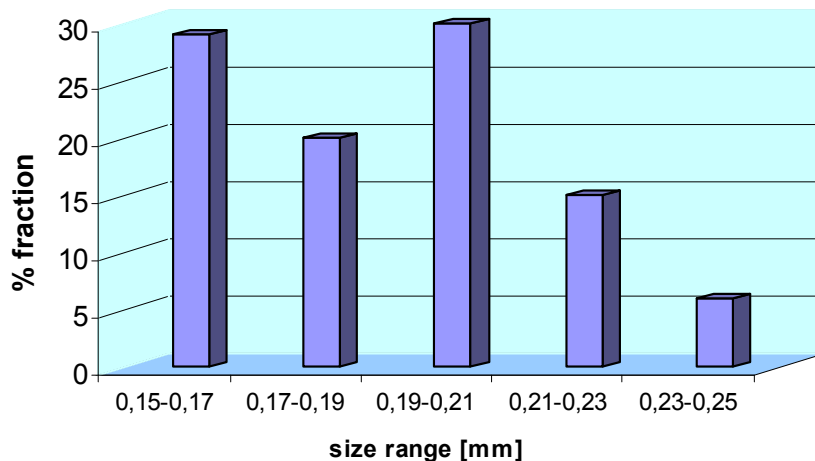


Fig. 3. Glass microglobules size distribution

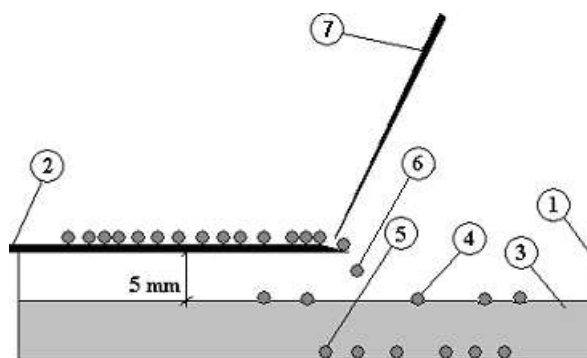


Fig. 4. Film flotation arrangement used in our investigation, 1 – glass vessel, 2 – horizontal plate, 3 – liquid being examined, 4 – floating particles, 5 – sinking particles, 6 – falling particle, 7 – needle

The reference liquid used for calculation of contact angle was determined using the film flotation method. It was assumed that the reference liquid - possessing ideal wetting ability (contact angle equal to zero) is that liquid for which 1% of microglobules remains at the surface.

The test was carried out by placing a single glass microglobule on liquid surface and the percent of floating particles out of 100 was determined. For each liquid three runs were practiced. The laboratory setup used for the experiments is shown in Fig. 4 and Fig. 5.

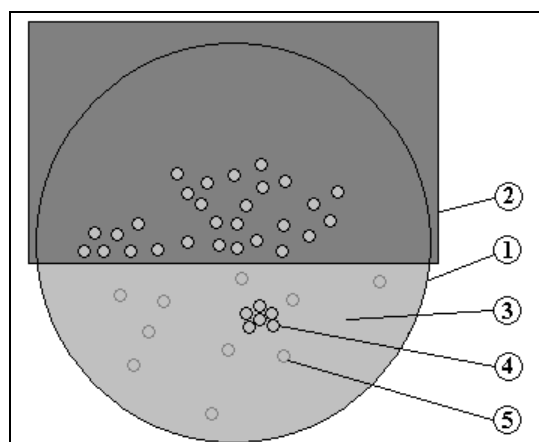


Fig. 5. Film flotation experiment arrangement - top view. 1 – glass vessel, 2 – horizontal plate, 3 – liquid being examined, 4 – floating particles, 5 – sinking particles, 6.

The experimental data for all investigated liquids are shown in Table 1. The capillary rise was determined using apparatus shown in Fig 6.

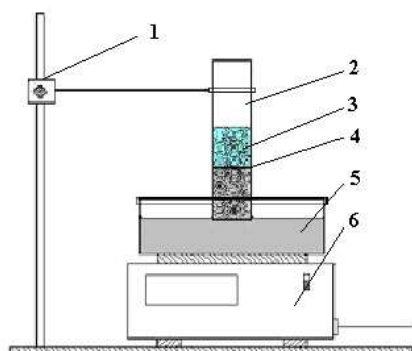


Fig. 6. Experimental setup for determining capillary rise: 1 - support, 2 - capillary, 3 – packing of glass microspheres, 4 - head of liquid, 5 - vessel with liquid, 6 – balance linked to computer (Trong and Hupka, 2005)

A computer program was used to register balance readings and the results were saved to a file. After the measurement, a plot was made for each liquid showing relation between squared mass increase v.s. time of penetration. The results obtained for the investigated and reference liquids are shown in Figs 7, 8, and 9. Based on the graphs, the time of penetration was found (39 s for methylene chloride, 49 s for water and 131 s for decane) and the contact angle for water and decane was calculated. Using Eq. (10) we obtain  $44.5^\circ$  for water and  $41.4^\circ$  for decane, and using mean radius of capillary (Eq. (3) and the Washburn equation we obtain  $43.5^\circ$  for water and  $40.2^\circ$  for decane.

Table 1. Liquids examined by film flotation method

Liquid	Surface tension, [mJ/m <sup>2</sup> ]	Viscosity [mPa·s]	Density [kg/m <sup>3</sup> ]	% flotating microglobules
Pentane	16.00	0.25	630	0
Isooctane	18.80	18.80	690	0
Heptane	19.30	0.42	710	0
Octane	21.80	0.55	700	0
Ethanol	22.00	1.20	0,81	0
Methanol	22.10	0.54	790	0
Acetone	22.68	0.30	790	0
Decane	23.90	0.93	726	0
n-butyl acetate	25.10	0.74	880	0
CCl <sub>4</sub>	26.95	0.90	1590	0
Toluene	27.80	0.55	870	0
Xylene	28.30	0.65	860	0
Cycloheksanone	34.00	2.20	950	0
Nitric acid	41.20	0.75	1526	0
2-propanol	18.30	2.07	780	1
Dichloromethane	27.20	0.42	1320	1
Ethylene bromide	38.40		2180	2
Nitromethane	36.20	0.61	1140	3
Pyridine	38.00	0.95	980	4
Water	72.30	1.00	998	13
Sulfur acid	55.10	24.54	1840	23
Hydrazine	91.50	0.91	1000	30
o-Toluidine	40.00		990	40
Aniline	42.90	4.40	1020	45
Oleic acid	32.50	39.00	890	81
Benzyl alcohol	39.00	5.04	1042	90
Hexanol	24.08	4.59	820	95
Ethylene glycol	47.00	21.00	1110	100
Glycerol	62.50	945.00	1260	100

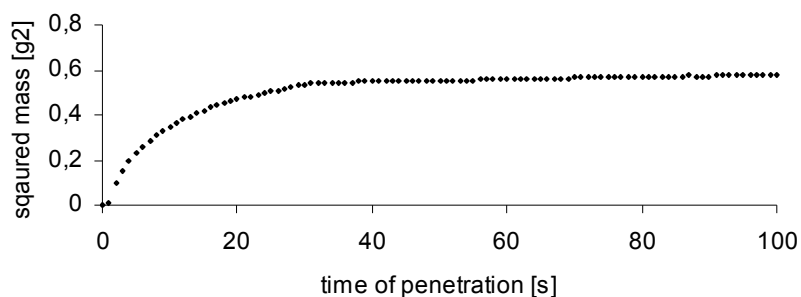


Fig. 7. The relationship between squared mass of methylene chloride (reference liquid) vs. time of penetration.



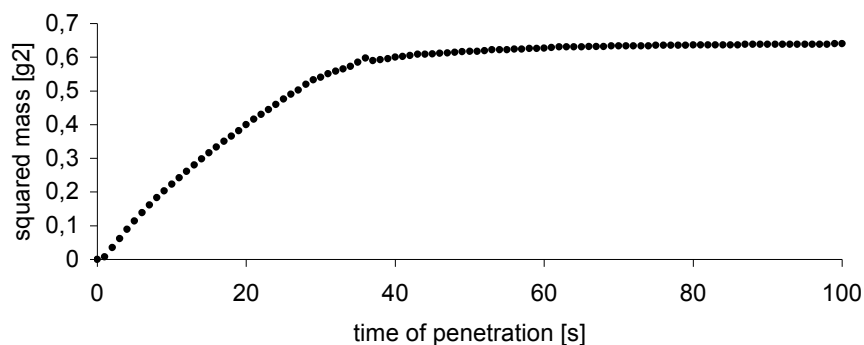


Fig. 8. The relationship between squared mass of water vs. time of penetration

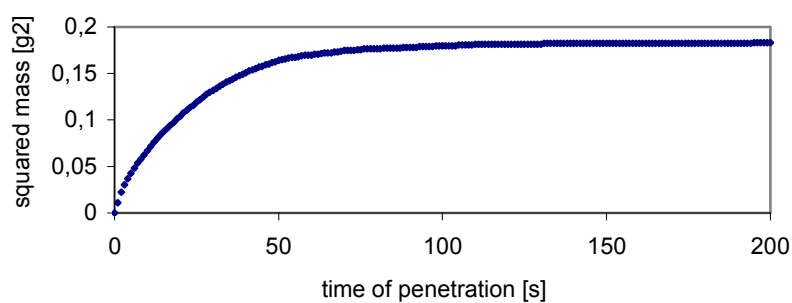


Fig. 9. The relationship between squared mass of decane vs. time of penetration

## FINAL COMMENTS

The capillary rise method employed for the investigation possesses many advantages, it is convenient and fast to use, does not require expensive and complex apparatus, measurement errors are minimized while changing the working conditions (ambient temperature), the results obtained possess error resulting only from non-linear changes of substance properties. The big disadvantage, however, is the necessity to choose a reference liquid - the one ideally wetting the material examined.

If another reference liquid, chosen depending on another criterion, had been used, the result would have been different. Moreover, if another liquids were examined they could prove to better wet loose material and the final result would also be different.



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## REFERENCES

- BARTELL F. E., WALTON C. W. Jr., Alteration of the surface properties of stibnite as revealed by adhesion tension studies, *J. Phys. Chem.*, 1934, 38, 503–511.
- BARTELL F. E., WHITNEY C. E., Adhesion tension. III, *J. Phys. Chem.*, 1932, 36, 3115-3126.
- CHURAEV N.V., Aqueous wetting films in contact with a solid phase, Preface, *Advances in Colloid and Interface Science*, 2005, 114-115, 3-7.
- DIGGINS D., FOKKINK L. G. S., RALSTON J., The wetting of angular quartz particle: capillary pressure and contact angles, *Colloid Surf. A*, 1990, 44, 299–313.
- FEURSTENAU D. W., DIAO J., WILLIAMS M.C., Characterization of the wettability of solid particles by film flotation. 1. Experimental investigation, *Colloid and Surfaces*, 1991, 60, 127-144.
- HAMRAOUI A., NYLANDER T., Analytical approach for the Lucas-Washburn equation, *J. Colloid Interface Sci.*, 250 (2002) 415–421.
- LEVINE S., LOWNDES J., WATSON E.J., NEALE G., A theory of capillary rise of a liquid in a vertical cylindrical tube and in a parallel-plate channel Washburn equation modified to account for the meniscus with slippage at the contact line *J. Colloid Interface Sci.* 1980, 73, 136.
- SIEBOLD A., NARDIN M., SCHULTZ J., WALLISER A., OPPLIGER M., Effect of dynamic contact angles on capillary rise phenomena, *Colloid Surf. A*, 2000, 161, 81–87.
- STUDEBAKER M. L., SNOW C. W., The influence of ultimate composition upon the wettability of carbon blacks, *Wettability of Carbon Blacks*, 59 (1955) 973–976.
- TRONG D. V., Charakterystyka układu porowatego metodą wzniesienia kapilarnego za pomocą równania Washburn'a, praca doktorska, Gdańsk 2005.
- TRONG D.-V., HUPKA J., Characterization of porous materials by capillary rise method, *Physicochemical Problems of Mineral Processing*, 2005, 39, 47-65
- WASHBURN E. W., The dynamics of capillary flow, *Phys. Rev.*, 1921, 17, 273–283.
- XU Z., MASLIYAH J. H., Contact angle measurement on oxide and related surfaces, in: *Encyclopedia of Surface and Colloid Science*, Hubbard A. (ed.), Marcel Dekker, New York 2002, 1228–1241.
- XUE H.T., FANG Z.N., YANG Y., HUANG J.P., ZHOU L.W., Contact angle determined by spontaneous dynamic capillary rise with hydrostatic effects: Experiment and theory, *Chemical Physics Letters*, 2006, 432, 326-330.

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Pośrednie metody oceny zdolności zwilżania drobnych cząstek lub materiałów porowatych wymagają wyboru cieczy odniesienia, dla której kąt zwilżania jest równy zero. W badaniach własnych zastosowano metodę wzniesienia kapilarnego oraz metodę flotacji filmowej dla układów mikrokulki szklane-woda i mikrokulki szklane-dekan. Uzyskane dane dla cieczy odniesienia i dla cieczy badanej wprowadzono do zmodyfikowanego równania Washburn'a i wyznaczano wartość kąta zwilżania.

*Słowa kluczowe: wzniesienie kapilarne, flotacja filmowa, materiały porowate, zwilżalność, kąt zwilżania*

