

WETTING CRITERIA FOR THE APPLICABILITY OF MEMBRANE DISTILLATION*

A.C.M. FRANKEN, J.A.M. NOLTEN, M.H.V. MULDER, D. BARGEMAN and C.A. SMOLDERS

Twente University, Department of Chemical Technology, P O Box 217, 7500 AE Enschede (The Netherlands)

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Summary

Membrane distillation can only be applied on liquid mixtures which do not wet a microporous hydrophobic membrane. Solutions of inorganic material in water have such high values of surface tension ($\gamma_L \geq 72 \times 10^{-3}$ N/m) that the non-wetting condition is fulfilled for a number of hydrophobic membranes. As soon as organic solutes are present in the solution, the surface tension γ_L will be lowered, and if the concentration of organic material becomes too high, wetting of the membrane will occur. By means of theoretical considerations a critical solute concentration or surface tension at which a homogeneous smooth material will be wetted ($\theta < 90^\circ$) can be calculated. For (micro)porous membranes no such theoretical relation can be derived. Therefore, a simple experimental method is described to measure the maximum allowable concentration for a (micro)porous membrane. On the basis of these measurements, the maximum allowable concentration under process conditions can be determined

Introduction

Membrane distillation is a distillation process which makes use of the pores of a microporous non-wettable membrane as the vapour phase. In this process two aqueous liquids with different temperatures are separated by a hydrophobic microporous membrane. The vapour pressure difference ΔP_v across the membrane, resulting from the temperature difference ΔT , causes vapour molecules to be transported through the pores of the membrane from the warm side (feed) to the cold side (permeate).

The advantages of membrane distillation are that the distillation process takes place at moderate temperature and that a relatively low temperature difference between the two liquids contacting the microporous hydrophobic membrane gives relatively high fluxes. Because entrainment of dissolved particles is avoided, a permeate with a high purity is obtained.

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However, membrane distillation is only possible if the restrictive condition is fulfilled that the pores of the membrane are not filled with liquid. Hence the wetting power of the liquids should be low. Water and solutions of inorganic substances in water have such high values of surface tension ($\gamma_L \geq 72 \times 10^{-3}$ N/m) that for a number of hydrophobic microporous membranes with pores in the range of $1 \mu\text{m}$ or less (such as polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE, Teflon)) this non-wetting condition is guaranteed. Therefore, important applications of membrane distillation can be seen in the field of water purification and in concentration of product solutions or waste water solutions [1, 2].

When organic solutes are present in an aqueous solution, the surface tension γ_L will decrease rapidly. If the concentration of organic material does not exceed a certain critical value (so that the liquid on both sides of the membrane does not wet the membrane), the membrane distillation process can still be used. On the other hand, if the concentration of organic material exceeds this critical value, the microporous membrane will be filled with liquid. In this case membrane distillation is no longer possible.

The aim of this investigation is to find out which concentration of organic material in water is allowed before the liquid will penetrate into the membrane.

Background

The value of the contact angle θ of a liquid droplet on an ideal smooth homogeneous surface is described by Young's equation:

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL} \quad (1)$$

A droplet of water on a hydrophobic surface (e.g. PP, PVDF or PTFE) will give a contact angle which is larger than 90° . If surface active agents (or in general: organic materials) are dissolved in water, the surface tension of the liquid will decrease. As a consequence, the contact angle θ will decrease, and if θ becomes smaller than 90° the liquid will wet the solid surface. In case the material is non-porous the contact angle will have a value between 0° and 90° . On the other hand, if the material is porous (which is the case for membranes used in the membrane distillation process) it is possible that the droplet will penetrate into the pores of the material.

Lucassen-Reynders [3] stated that any of the interfacial tensions in eqn. (1) can be affected by surfactant adsorption by virtue of Gibb's law:

$$\frac{d\gamma_i}{d(\ln a_i)} = -RT\Gamma_i \quad \text{with } i = L, S, SL \quad (2)$$

a_i being the activity of the surfactant and Γ_i its surface excess at any interface.

Adsorption of surfactants can only influence the contact angle if they affect the ratio $(\gamma_S - \gamma_{SL})/\gamma_L$. Changes in contact angle can be shown conveniently

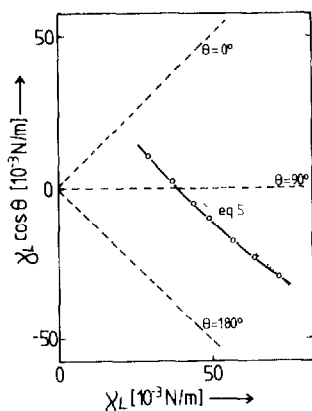


Fig. 1 $\gamma_L \cos \theta$ as a function of γ_L for ethanol-water mixtures on a homogeneous PTFE surface, the dotted line is calculated according to eqn. (5)

by plotting $(\gamma_S - \Gamma_{SL})$ as a function of γ_L . Combination of eqns. (1) and (2) then yields the following expression:

$$\frac{d(\gamma_L \cos \theta)}{d\gamma_L} = \frac{\Gamma_S - \Gamma_{SL}}{\Gamma_L} \quad (3)$$

For low energy surfaces (such as PP, PVDF or PTFE) it is expected that hardly any interaction exists between the surface active agents and the surface, in which case $\Gamma_{SL} \approx \Gamma_L$. It is also expected that $\Gamma_S \ll \Gamma_{SL}$ [4], and consequently the slope of the curve as represented by eqn. (3) will be

$$\frac{d(\gamma_L \cos \theta)}{d\gamma_L} \approx -1 \quad (4)$$

Bargeman and Van Voorst Vader [4] indeed found this relation for solutions of sodium decane-1-sulphonate and sodium dodecane sulphate in water on non-polar solids such as paraffin wax and PTFE. For conditions as assumed up till now the influence of surfactants on the contact angle on non-polar solids can be described by

$$\gamma_L \cos \theta = -\gamma_L + C \quad (5)$$

This linear equation with a slope equal to -1 has the advantage that only one contact angle measurement needs to be performed: the measurement of the contact angle of pure water on the solid material. If the surface tension of the solution as a function of the composition is known, the value of γ_L and therefore the value of the contact angle θ can be calculated for each solution composition. This situation is represented by the dotted line in Fig. 1.

In Figure 1 the value of γ_L^{90} is given by the intercept on the abscissa. γ_L^{90} is the surface tension of a liquid mixture which has a contact angle of 90° when

brought in contact with a homogeneous smooth solid material. In the membrane distillation process the value of γ_L^{90} is very important. If the surface tension of a liquid is lower than γ_L^{90} it may be possible for the liquid to penetrate into the pores of the porous material spontaneously.

The surface tension of a liquid which is on the verge of penetration into the pores of a (micro)porous membrane is defined as γ_L^p (p stands for penetration). As far as membrane distillation is concerned the value of γ_L^p is even more important than the value of γ_L^{90} .

Although the above described method for the determination of γ_L^{90} seems to be promising, it cannot be used as an accurate determination of γ_L^p . This is mainly due to three effects:

1. The experimental error for points on a line with a certain inaccuracy in its slope drawn through one experimental point with a certain inherent error increases with the distance to that point.
2. The use of eqn. (5) is limited to surface active agents of a certain molecular structure (rather long chain amphipolar molecules, so called surfactants).
3. The value of γ_L^{90} does not always coincide with the value of γ_L^p for porous media.

Re 1. Although contact angle measurements can be made very accurately some deviations are inevitable. Mostly a deviation of about 1° is given. In literature the differences between the measured contact angles may differ considerably. For example, for a droplet of water on a Teflon surface, contact angles varying from 108° to 115° have been reported [5–8]. This effect is mainly due to the use of different specimens of Teflon. Another source of error is the inaccuracy in the slope of the curve: the slope is not exactly -1 . For different series of measurements Bargeman and Van Voorst Vader [4] found that the slope varied between -0.96 and -1.02 . Therefore, the effect of an experimental error in the contact angle is reinforced by the uncertainty in the tangent of the slope. For example, if for a droplet of water on Teflon a contact angle $\theta = 114^\circ \pm 1^\circ$ is found and the tangent of the slope is uncertain within 2%, then the extreme values for γ_L^{90} are 40×10^{-3} N/m and 46×10^{-3} N/m, respectively

Re 2. Equation (5) is used to describe the influence of surfactants on the contact angle of non-polar solids, and a good agreement with experimental results is found [4]. On the other hand, this relation cannot be used in general for mixtures of water and low molecular weight organic components, such as alcohols (methanol, ethanol) or carboxylic acids (formic acid, acetic acid). In these cases a linear behaviour as described by eqn. (5) is not always found. As an example the curve for ethanol/water mixtures on a homogeneous PTFE surface is given in Fig. 1 (the experimental results were obtained from Bennett and Zisman [6]).

Re 3. The difference between γ_L^{90} and γ_L^p will be demonstrated and explained on the bases of the results of our experiments.

The restrictions mentioned above do not permit an accurate determination of γ_L^{90} on the basis of the measurement of the contact angle of a droplet of water on a solid. Furthermore it is doubtful whether the value for γ_L^{90} is identical to that for γ_L^E .

From the above considerations it can be concluded that the value of γ_L^E has to be determined experimentally for the microporous membrane used.

Method of investigation

Determination of γ_L^E

The value of γ_L^E is determined by the 'penetrating drop method'. In this method a droplet is brought in contact with the (micro)porous membrane. By trials with narrowing series of solution compositions the composition of a liquid mixture is determined at which the liquid is on the verge of penetration into the membrane. The amount of organic material in water at this composition is called the 'maximum allowable concentration' and γ_L^E is defined as the value of the surface tension belonging to this composition. The advantages of the penetrating drop method are:

- the value of γ_L^E can be measured directly,
- the measurements can be carried out on the membrane material itself,
- the method is experimentally simple and requires no special equipment,
- the measurements can be carried out very quickly,
- the method has a high accuracy (compared to the contact angle measurement).

The accuracy of the penetrating drop method can be illustrated by the following example. A droplet will have a height of less than 5 mm and therefore will exert a gravitational force of about 50 N/m^2 , which might form an inaccuracy in determining γ_L^E . Suppose the maximum pore size of the membrane material is smaller than $10 \mu\text{m}$. According to the Laplace equation,

$$\Delta P = - \frac{2B\gamma_L \cos\theta}{r_{\max}} \quad (6)$$

the value of $\gamma_L \cos\theta$ can be measured with an accuracy of less than $0.25 \times 10^{-3} \text{ N/m}$. In the above equation B is a pore geometry coefficient, being 1 for cylindrical pores. Using eqn. (4) for an estimation of the uncertainty in γ_L^E , in this case $\Delta\gamma_L^E$, it follows that $\Delta\gamma_L^E < 0.25 \times 10^{-3} \text{ N/m}$.

Calculation of γ_L^E under process conditions ($\gamma_{L,pc}^E$)

The preceding explanation of γ_L^E and its determination is only partly appli-

cable to hydrophobic microporous membranes under process conditions. As far as intrinsic membrane properties are concerned the preceding discussion remains unaltered.

Nevertheless, it can be easily understood that a liquid mixture with a composition just beneath the maximum allowable concentration can give problems in the membrane distillation process. In practical applications the pressure, exerted by the liquid on the membrane, will be higher than zero as a result of, among other things, pumping pressure. If in that case the liquid has a surface tension γ_L which is only slightly higher than γ_L^p , it is possible that the liquid penetrates into the microporous membrane.

Therefore, $\gamma_{L,pc}^p$ is introduced. The surface tension $\gamma_{L,pc}^p$ is defined as the 'minimum allowable surface tension under process conditions'. The concentration corresponding to $\gamma_{L,pc}^p$ is called 'maximum allowable concentration under process conditions'.

The relation between the applied pressure and the surface tension is given by the Laplace equation (eqn. 6). If the value of the maximum pore size is known and an estimation is made of the applied pressure, then the value of $\gamma_L \cos\theta$ can be calculated. If the curve for $\gamma_L \cos\theta$ as a function of the concentration is known, then the value of $\gamma_{L,pc}^p$ can be obtained graphically. Determination of $\gamma_{L,pc}^p$ in this way makes use of the assumption that $\gamma_L^{90} = \gamma_L^p$ and, as will be shown later, this assumption is not always correct.

A better approach is provided by making use of eqn. (5). Combination of this equation and eqn. (6) with the boundary condition $\gamma_L = \gamma_L^p$ if $\gamma_L \cos\theta = 0$, yields the following equation:

$$\gamma_L = \gamma_L^p + \frac{\Delta P r_{\max}}{2B} \quad (7)$$

If in the above equation the values for a membrane distillation process are substituted, the calculated value of γ_L is equal to $\gamma_{L,pc}^p$. For a proper use of eqn. (7) it is important that the value of ΔP which is substituted is higher than the maximum pressure to be applied to the system.

Experimental determination of $\gamma_{L,pc}^p$

The above calculation of $\gamma_{L,pc}^p$ reproduces reliable results. If, however, an accurate determination of $\gamma_{L,pc}^p$ is desired, the value of $\gamma_{L,pc}^p$ has to be determined experimentally.

This can be done by determining the 'liquid entry pressure' as a function of the surface tension of the liquid (in other words: as a function of the concentration of organic material in water). For these measurements a dry microporous membrane is put into a cell and the liquid is brought into contact with the membrane. The liquid is put under pressure and this pressure is slowly raised. The pressure at which the liquid penetrates into the membrane is defined as the liquid entry pressure. By changing the liquid composition, the liquid entry

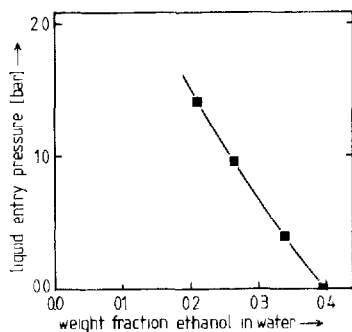


Fig. 2. Liquid entry pressure as a function of the weight fraction of ethanol in water for a flat PP membrane (Accurel 0.1).

pressure is obtained as a function of the concentration of organic material in water. In order to minimize the number of experiments, the calculated value of $\gamma_{L,pc}^L$ can be used as a first estimate. In Fig. 2 the liquid entry pressure is given as a function of the weight fraction of ethanol in the mixture, using a microporous polypropylene membrane (Accurel 0.1).

Note that at the point where the liquid entry pressure is zero, the concentration is equal to the maximum allowable concentration, and the surface tension of the liquid is equal to γ_L^L .

Of course, a margin of safety should be taken. The point of operation should always be situated on the left-hand side of the curve in Fig. 2 and preferably not too close to this curve.

Summary of the method

The experimental method involves the following steps:

- determination of γ_L^L by means of the 'penetrating drop method'
- calculation of $\gamma_{L,pc}^L$ by means of eqn. (7), in which $\gamma_L = \gamma_{L,pc}^L$
- determination of the 'liquid entry pressure' as a function of the liquid composition (in case the calculation of $\gamma_{L,pc}^L$ is not accurate enough).

Experimental

We have seen that in this investigation two different experimental techniques were used, namely:

- the penetrating drop method,
- the liquid entry pressure method.

Both techniques are rather simple and have already been described in the previous paragraph.

Penetrating drop method (PDM) measurements were carried out using two different kinds of polymers (PVDF and PP) with different characteristics. An overview of the characteristics of the membranes used is given in Table 1.

TABLE 1

Properties of membranes used

Property	Acc. 0.1	R 5/1	PV 159	F 0030
Material	PP	PP	PVDF	PVDF
Configuration	flat	cap. ^a	cap. ^a	cap. ^a
Outer diameter (μm)	—	1800	1230	1500
Inner diameter (μm)	—	1200	830	1000
Membrane thickness (μm)	160	300	200	250
Porosity (%)	ca. 80	ca. 80	75	82
Av. pore diameter (μm)	0.1	0.1		
Max. pore diameter (μm)	0.40	0.3	0.25	0.60

^aCapillary

Liquid entry pressure (LEP) measurements were carried out on flat PP membranes and on capillary PVDF membranes. Both PDM measurements and LEP measurements were conducted with new untreated membranes which were only used in one experiment. All the membranes were kindly supplied by Enka A.G. (Product Group Membrana).

Results

In this section the results of the penetrating drop method and the liquid entry pressure measurements will be presented. In order to be able to compare the results of these measurements with the results of measurements on homogeneous, smooth surfaces, the literature results for the latter are presented in Table 2. In this table the results of measurements on PTFE surfaces are also given.

The results of the penetrating drop method measurements are given in Table 3, and some of these measurements are also plotted in Fig. 3 and 4. Although the values obtained for γ_L^0 deviate strongly from γ_L^{90} , some interesting conclusions can be drawn from these measurements.

First, it is remarkable that the liquid penetrates into PVDF membranes at a

TABLE 2

Some properties of hydrophobic materials

Property	PP	PVDF	PTFE
γ_L^{90} (10^{-3} N/m)	55	50	40.5 [6]
γ_c (10^{-3} N/m) ^a	29 [10]	25 [9]	18 [9]

^a γ_c is the critical surface tension of wetting of a homogeneous smooth material by a liquid mixture, which is defined by the intercept of the experimental line in Fig. 1 with the line where $\theta = 0$ [9]

TABLE 3

Penetrating drop measurements of aqueous mixtures of organic components

Organic component	Membrane							
	PV159		F 0030		R 5/1		Acc. 0.1	
	wt. %	γ_L^p	wt. %	γ_L^p	wt. %	γ_L^p	wt. %	γ_L^p
Methanol	37	37.8	35	38.5	69	29.0	74	28.0
Ethanol	23.5	36.5	21	38.0	35	31.5	41	29.5
1-Propanol	11.5	33.5	10.5	35.0	13	32.0	15.5	29.5
1-Butanol	4.5	31.0	3.5	32.0	4.5	31.0	5.5	29.0
2-Butanol	9	29.0	7.5	31.0	8.5	29.5	9	29.0
Formic acid	59	47.5	53	48.9	100	—	100	—
Acetic acid	31	43.4	27	44.7	81	32.2	83	31.8
Propionic acid	17	39.0	15.5	39.8	37	33.3	43	32.5
Butyric acid	5	38	5	38	9	32.5	9	32.5
DMAc	41	48	39	50	91	36	94	35.5
DMF	43	48	39	50	95	36	98	35.5
DMSO	61	50	57	51	100	—	100	—
Acetone	33	35.0	31	35.8	47	31.2	54	29.8
1,4-Dioxane	37	44.3	35	45.0	61	38.2	64	37.7

For PVDF as membrane material (PV 159 and F 0030) · $\gamma_L^{90} = 50 \times 10^{-3}$ N/m; for PP (R 5/1 and Acc. 0.1) $\gamma_L^{90} = 55 \times 10^{-3}$ N/m.

higher value of γ_L than for penetration into PP membranes. This result is unexpected since PVDF is a more hydrophobic material than PP.

The second conclusion which can be obtained from these measurements is that all the values of γ_L^p are lower than the value of γ_L^{90} . Some of the measurements (e.g. alcohol-water mixtures in contact with flat PP membranes) give values for γ_L^p which are almost as low as γ_c . This means that contact angle measurements on homogeneous smooth materials form no good criterion at all for the applicability of membrane distillation. The only measurements in which values of γ_L^p are roughly equal to γ_L^{90} are the experiments with aqueous mixtures of DMF, DMAc and DMSO on PVDF porous membranes; however, even for different types of PVDF membranes differences occur.

The third conclusion that can be drawn from the PDM experiments is that for a specific membrane γ_L^p can be dependent upon the composition of the liquid mixture. For PP membranes the value of γ_L^p seems to be dependent upon the class of organic solutes only and not on the molecular size within a series. For instance, for a flat PP membrane (Accurel 0.1) the following values for γ_L^p are found:

alcohols $\sim 29 \times 10^{-3} \text{ N/m}$
 carboxylic acids $\sim 32 \times 10^{-3} \text{ N/m}$
 DMF/DMAc $\sim 36 \times 10^{-3} \text{ N/m}$

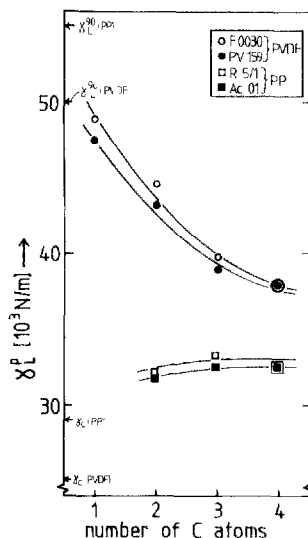
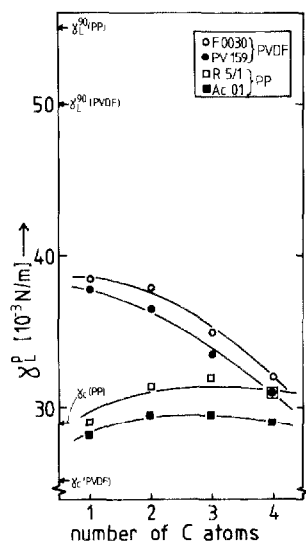


Fig. 3. γ_L^P for aqueous mixtures of alcohols; on the x -axis the number of carbon atoms of primary alcohols is plotted.

Fig. 4. γ_L^P for aqueous mixtures of carboxylic acids; on the x -axis the number of carbon atoms of primary carboxylic acids is plotted.

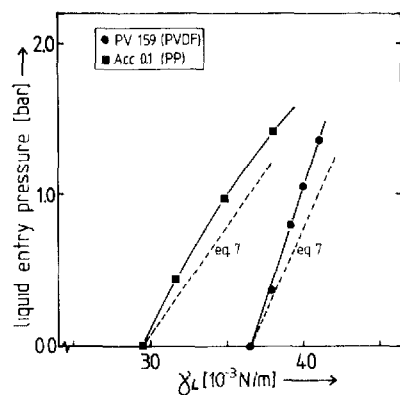


Fig. 5. Liquid entry pressure as a function of the surface tension of the liquid mixture of ethanol and water; the dashed lines are calculated by means of eqn (7)

On the other hand, for PVDF membranes this dependence is different. Both for a series of aqueous mixtures of alcohols and for a series of aqueous mixtures of carboxylic acids the values of γ_L^p decrease when the number of carbon atoms increases (see also Figs. 3 and 4).

Liquid entry pressure measurements were carried out to find out whether the values of the PDM measurements and the use of these values for the calculation of $\gamma_{L,pc}^p$ by means of eqn. (7) are correct. The LEP measurements were carried out on flat PP membranes and on capillary PVDF membranes with aqueous mixtures of ethanol. The results of the measurements are given in Fig. 5. In this figure the LEP value is plotted as a function of the surface tension of the aqueous ethanol mixture. The values of $\gamma_{L,pc}^p$ which are calculated by means of eqn. (7) are represented in Fig. 5 by dashed lines.

From this figure it can be seen that:

- The value of γ_L^p , measured by the PDM, is in good accordance with LEP measurements.
- The values of $\gamma_{L,pc}^p$ which are calculated by eqn. (7) differ from the values measured by means of the LEP. A reason for this deviation might be that $d(\gamma_L \cos\theta)/d\gamma_L$ is not exactly -1 . Furthermore, the membrane structure might be a factor of importance.
- The slope of the LEP curve is not constant. This means that the use of eqn. (7) is limited, as was already discussed before. The deviation might be caused by the fact that ethanol is not a surfactant and its mixtures with water are far from ideal.

In spite of the slight difference between the measured and the calculated curves it can be concluded that the description of the wettability criteria for a membrane distillation system by means of the penetrating drop method and the calculation of the values of $\gamma_{L,pc}^p$ are rather good.

Discussion

From the results that are presented here it becomes clear that the calculation of a maximum allowable concentration of organic material on the basis of simple contact angle measurements of a droplet on a homogeneous material is not possible. The measured values of γ_L^{90} obtained in that way cannot be used to describe the penetration of a liquid into a porous material. The values of γ_L^p , measured by means of the PDM, are lower than γ_L^{90} and higher than γ_c , and their exact value can only be obtained by measurement.

In this paragraph a qualitative explanation for the difference between the values of γ_L^p on one hand and γ_L^{90} and γ_c on the other will be given. The value of γ_L^p will depend upon the polymer material, the porous structure of the membrane, and the composition of the liquid (mixture). The value of γ_L^{90} (and γ_c) depends upon the polymer material and in some cases also on the composition of the liquid (mixture). For instance, Bennett and Zisman [6] found different values for γ_c of polyethylene when measured with different aqueous solutions

TABLE 4

Contact angle on a smooth surface (θ) for which a porous substrate with pore fraction f_2 will be wetted ($\theta' = 90^\circ$)

f_2	θ ($^\circ$)	f_2	θ ($^\circ$)
0	90	0.45	35
0.2	75	0.48	23
0.4	48	0.5	0

(PE: γ_c (ethanol, 1-butanol) = 27.5×10^{-3} N/m; γ_c (1,4-dioxane) = 31.5×10^{-3} N/m). Although no other values for PP and PVDF are known except for the ones given in Table 2, it is expected that γ_c might be slightly different for different liquid mixtures in contact with these materials.

However, the above explanation for the possible difference in γ_c does not explain why the value of γ_L^p is (much) lower than γ_L^0 . This experimental fact can be explained by the extremely high surface porosity of the membrane material. Davies and Rideal [11] stated that on rough or hairy surfaces always higher contact angles are obtained than on a smooth surface of the same material. This can be understood by the following relation, derived by Cassie and Bacter [12]:

$$\cos\theta' = f_1 \cos\theta - f_2, \quad (8)$$

which gives a relation between the contact angle measured on a rough surface (θ') and the contact angle measured on a smooth surface (θ). In eqn. (8) f_1 and f_2 are the fractions of the composite surface which are liquid–solid and liquid–air respectively. This equation can only be used if $f_2 < f_1$. In the other case ($f_2 > f_1$) $\cos\theta'$ would be smaller than zero, which means that θ' is always larger than 90° . This should mean that such a surface could never be wetted. However, it can be easily understood that, if θ becomes zero or approaches zero, the surface of the material (even inside the pores) becomes completely wetted.

For highly porous membranes, like the ones that are used in our investigations, the value of f_2 will be substantial and may even be larger than 0.5, in which case eqn. (8) is no longer valid. (Note: the fact that the overall porosity of a membrane is 80% does not mean that f_2 is equal to 0.8; probably this value is much lower.) In cases where eqn. (8) is valid, θ' is a function of the porosity.

In case of membrane distillation the membrane will be wetted only if $\theta' < 90^\circ$. For different values of f_2 , the contact angles on a smooth surface, θ , are listed in Table 4. The values in this table are calculated by means of eqn. (8) with the boundary condition $\cos\theta' = 0$. From this table it can be seen that for f_2 in the range of 0.45–0.5 a small variation in porosity (or better: in liquid–air

surface fraction) leads to an enormous difference in required contact angle, and will also lead to differences in γ_L^p .

It should be mentioned again that not all the results can be explained by this qualitative description. For instance, the fact that γ_L^p for alcohols and carboxylic acids on PVDF membranes is lowered as the number of carbon atoms increases, whereas the values on the PP membranes remain constant, cannot be explained by the above discussion. Therefore, further investigations, especially on the influence of membrane structure on wetting phenomena, will be carried out.

Conclusions

The main conclusion that can be drawn from our investigations is that the maximum allowable concentration of organic material in water cannot be calculated, but has to be determined experimentally.

The 'penetrating drop method' is a good and experimentally simple method for determining the maximum allowable concentration of organic material in water and its corresponding surface tension, γ_L^p .

The semi-empirical way to determine the surface tension at process conditions, $\gamma_{L,pc}^p$, making use of the penetrating drop method and eqn. (7) gives fairly good results, which can be used to safely estimate the maximum allowable concentration at process conditions.

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List of symbols

a	activity of surfactant (—)
B	pore geometry coefficient (—)
C	(eqn. 5) constant (N/m)
f_1	(eqn. 8) liquid–solid surface fraction (—)
f_2	(eqn. 8) liquid–air surface fraction (—)
ΔP	pressure difference (N/m ²)
ΔP_v	vapour pressure difference (N/m ²)
R	gas constant ($\equiv 8.310 \text{ J/mol} \cdot ^\circ\text{C}$)
r_{\max}	maximum pore radius (μm)
ΔT	temperature difference ($^\circ\text{C}$)
Γ	surface excess activity of surfactant (mol/m ²)

γ	surface tension (N/m)
γ_c	critical surface tension of wetting (N/m)
γ_L^{90}	surface tension of a liquid (mixture) which has a contact angle of 90° when brought in contact with a homogeneous smooth solid material (N/m)
γ_L^p	surface tension of a liquid (mixture) that is on the verge of penetration into the pores of a (micro)porous membrane (N/m)
$\gamma_{L,pc}^p$	γ_L^p under process conditions (N/m)
θ	contact angle ($^\circ$)
θ'	(eqn. 8) contact angle on a rough surface ($^\circ$)

Subscripts

i	index
L	liquid
S	solid
SL	solid-liquid

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