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Solid–gas mass transfer measurement by the swollen polymer method: proving of swelling agents

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Abstract—There are here identified a number of new swelling agents, i.e. transferring species—hexadecane, tetradecane, dodecane, 1-methylnaphthalene—for use in Macleod's swollen polymer method for the measurement of solid–fluid mass transfer rates. Their diffusivities in air and their vapour pressures (save for hexadecane) are determined. The swelling agent previously used most commonly has been ethyl salicylate; it is demonstrated that the literature value of its vapour pressure (in the range 20–40°C) is 25% too high. After this correction, consistent *j*-factors for mass transfer from the wall of a short pipe are obtained, independent of the swelling agent used.

INTRODUCTION

THIS work forms part of a study of heat transfer at the wall of packed beds of geometry typical of catalytic reactor tubes [1]. Since contributions to heat transfer there occur both by conduction across particles and by convective transport, the use of a mass transfer analogue to study the latter mechanism alone is apt. The chosen technique is the swollen polymer method of Macleod and his students [2–5]: this involves applying a thin (ca. 10^{-4} m) coating of a polymer to the wall and swelling it to equilibrium with a suitable swelling agent (SA). The mass transfer experiment consists of evaporating (or dissolving) the SA from the coating. There exists a *constant rate period* during which the evaporation rate is governed by the fluid-side resistance, not by resistance within the coating, and the equilibrium partial pressure of the swelling agent at the surface of the coating is insensibly different from its saturation vapour pressure.

Since measurement of transfer rate is here by repeated weighings of the test section, it is desirable that the constant rate period last at least 30 min. Accuracy requires that the experimental weight loss be large. Together, these require identification of swelling agents of high swelling power and suitable, and *known*, volatility. In particular, the swollen polymer method requires more accurate vapour pressure data than the other purposes to which such data are often put. It is further desired that the swelling agents be readily available at adequate purity and low cost and, ideally, that they should not degrade with time. Of the swelling agents used before [2–4], isobutyl benzoate was judged too dear, methyl salicylate too volatile and ethyl salicylate too volatile for use in the higher part of the Reynolds number range of interest. The work of identification described below should be of substantial use to those considering the use of this versatile, elegant and powerful technique.

PRELIMINARY IDENTIFICATION OF SWELLING AGENTS

The polymer used is polydimethylsiloxane (PDMS) available commercially as RTV 615 from the General Electric Corporation (U.S.A.). Application [1] of a scheme for prediction of solubility parameters, due to Small [6] and Hoy [7], yields a judicious choice of swelling agents expected to have high swelling power—it was concluded that hydrocarbons, halogenated hydrocarbons and the esters of straight chain fatty acids showed promise. Swelling experiments with these and a range of other compounds were performed using coated microscope slides. As Table 1 shows, the alkanes tried were particularly suitable, so that hexadecane and dodecane were also adopted for use.

Accordingly it was decided to perform preliminary mass transfer experiments in open tubes—that is, short (ca. 12 cm) unpacked lengths of stainless-steel pipe of o.d. 3.175 cm and i.d., when coated, of 2.96 cm. Into them was introduced a metered flow of laboratory compressed air which had been passed through filters and dried over silica gel, and whose temperature was measured to ±0.1°C accuracy. Intermittent removal and weighing of the pipe section determined the rate of weight loss during the constant rate period, from which the wall mass transfer coefficient was calculated using the logarithmic mean driving force. The outlet partial pressure was calculated by material balance. Experimental details are described elsewhere [1]. Table 2 shows that the values of mass transfer coefficient thus determined, when made dimensionless as *j*-factors, agreed well for

NOMENCLATURE

A_a	area of aperture [$\mathrm{m^2}$]
A, B, C	constants in the Antoine equations
A', B'	constants in the Clapeyron equations
D	diffusivity of the swelling agent vapour in air [$\mathrm{m^2\,s^{-1}}$]
d_o	diameter of the open tube [m]
d_p	diameter of the particles in the packed bed [m]
G	rate of loss of mass [$\mathrm{g\,s^{-1}}$]
k_G	mass transfer coefficient [$\mathrm{m\,s^{-1}}$]
K	$1/(1+0.5l/r)$
l	thickness of lid [m]
M	molecular weight (relative molar mass)
P	(saturated) vapour pressure of the swelling agent [$\mathrm{N\,m^{-2}}$]
r	radius of the circular aperture [m]
S_w	mass of swelling agent per unit mass of polymer [%]
T	temperature [K]
t	temperature [°C]
u	(superficial) air velocity [$\mathrm{m\,s^{-1}}$].

Greek symbols

ρ	density of air [$\mathrm{kg\,m^{-3}}$]
μ	viscosity of air [$\mathrm{kg\,m\,s^{-1} = N\,s\,m^{-2}}$].

Dimensionless groups

j_D	$(k_G/u)Sc^{2/3}$
Re, Re_p	Reynolds number, $\rho u d_o/\mu, \rho u d_p/\mu$
Sc	Schmidt number, $\mu/\rho D$.

hexadecane, tetradecane and 1-methylnaphthalene and were only a few percent high for dodecane. However, the values for ethyl salicylate were some 25% low. Because this latter is the most-used SA in work reported in the literature [2–5, 8–13], this discrepancy demands explanation.

DETERMINATION OF GAS-PHASE DIFFUSIVITIES

Since the definition of *j*-factor includes the Schmidt number, it was conceivable, though scarcely likely, that errors in the calculation of the diffusivity of ethyl salicylate in air caused some part of the discrepancy. So a simple check on the diffusivities of 1-methylnaphthalene, tetradecane and ethyl salicylate was made, using a Stefan experiment. This consisted of timing weight losses from a tall, narrow measuring cylinder containing a pool of SA to various depths [14]. The experiments were performed at temperatures between 375 and 425 K, in order that the mass flux should be large enough to be determined accurately, and because vapour pressure data for the SAs used were available in that temperature range. Admittedly, this later necessitates modest extrapolation of the diffusivity down to ca. 300 K. However, the purpose of these experiments was simply to establish the validity of the diffusivity predictions. Once this had been done at the higher temperatures, it was judged safe to use the formula under ambient conditions.

In Table 3, the results of these experiments are compared with the predictions given by the method reported in Bird *et al.* [15]. The agreement is as good as could have been hoped for, considering the crude experimental method. It is sufficient to rule out the diffusivity as the main source of the discrepancy in the swollen polymer mass transfer results. It is concluded that the literature values of the vapour pressure of dodecane and, more importantly, ethyl salicylate are the source of error.

DETERMINATION OF VAPOUR PRESSURES

The need for more reliable vapour pressure data at the temperatures of the mass transfer experiments has been demonstrated. It is a feature of some compilations of such data, however, that the values listed are smoothed mean values from a number of separate sources and the use of a standard table for all compounds may mean that the actual measured range is not apparent. Some of the tabulated figures may thus be extrapolated values and their precision less than that of others. Similarly, the precision of extrapolation beyond the tabulated range is very uncertain. As the bulk of reported measurements are at temperatures where the liquids are fairly volatile, the accuracy of extrapolations down to ambient temperature is unreliable, as is apparent in the following short review of literature for the compounds studied in this work.

This situation led Kapur and Macleod [16] to carry out measurements on ethyl salicylate at ca. 20°C by holographic and gas transpiration methods. Results by the former method were shown to lie very close to the line defined by the equation

$$\begin{aligned} P/\mathrm{N\,m^{-2}} &= 133.3(P/\mathrm{mmHg}); \\ \ln P/\mathrm{mmHg} &= 20.318 - 6790.7/T \end{aligned} \tag{1}$$

and are claimed to be within ±3% of extrapolated literature data [17]. The value at 20°C on their line (7.73 $\mathrm{N\,m^{-2}}$; 0.058 mmHg) is, however, 10% greater than the literature extrapolation (7.07 $\mathrm{N\,m^{-2}}$; 0.053 mmHg). It may be noted that the mean line through both of their sets of points is clearly slightly lower than equation (1) and we feel that their overall

Table 1. Physical properties of swelling agents and polymer/swelling agent systems

Swelling agent (SA)	Boiling point, T_b (°C)	Density, ρ_{SA} (g cm^{-3})	Molecular weight, M	Weight % swelling, S_w	Accept or reject	Reasons for rejection	
Ethyl salicylate	234	1.136^{15}	166.17	19.0 ± 0.3	A		
Ethyl caprate	244.6	0.859^{28}	200.31	50.3 ± 1.4	R	S.V.P. unknown	Limited shelf life; many need to be kept refrigerated
Ethyl laurate	269	0.868^{13}	228.36	43.5 ± 1.2	R	S.V.P. unknown	
Diethyl phthalate	299	1.121^{25}	222.23	3.5 ± 0.5	R	Low swelling power	
Isopropyl myristate	—	0.8532^{20}	270.44	37.9 ± 0.9	R	S.V.P. too low	
Methyl laurate	262	0.8702^{20}	214.34	50.7 ± 1.8	R	S.V.P. unknown	
n-Tetradecane	253	0.765^{20}	198.38	37.8 ± 1.3	A		
n-Pentadecane	270.5	0.770^{20}	212.41	34.7 ± 1.1	A		
Hexadec-1-ene	284.4	0.7811^{20}	224.44	35.0 ± 1.1	R	S.V.P. unknown	
1-Methylnaphthalene	244.6	1.025^{14}	142.19	18.8 ± 0.7	A		
1-Bromotetradecane	307	1.017^{20}	277.30	27.6 ± 0.5	R	S.V.P. unknown	
Caprylic acid	238	0.910^{20}	144.21	25.5 ± 0.5	R	S.V.P. unknown, corrosive	
Decyl alcohol	233	0.830^{20}	158.28	5.0 ± 0.3	R	Low swelling power	
2-Undecanene	228	0.828^{20}	170.29	42.0 ± 1.2	R	S.V.P. too high	

Density is at temperature (°C) indicated by superscript.
Density of polymer = 1.02 g cm^{-3}.
Ranges are 95% confidence intervals.

Table 2. Results of open-tube mass transfer experiments

				Averages	
Swelling agent	No. of runs	*Sc*	*Re*	j_D (using literature data)	j_D (using new data)
Ethyl salicylate	3	2.86	6070	4.93×10^{-3} (3)	6.69×10^{-3}
1-Methylnaphthalene	3	2.59	6080	6.82×10^{-3} (22)	6.66×10^{-3}
Tetradecane	2	3.51	6090	6.84×10^{-3} (20)	6.55×10^{-3}
Dodecane	2	3.19	6090	7.03×10^{-3} (20)	6.43×10^{-3}
Ethyl salicylate	1	2.86	14180	4.13×10^{-3} (3)	5.59×10^{-3}
1-Methylnaphthalene	1	2.59	14130	5.66×10^{-3} (22)	5.60×10^{-3}
Tetradecane	1	3.52	14160	5.63×10^{-3} (20)	5.40×10^{-3}
Hexadecane	2	3.88	14290	5.62×10^{-3} (30)	—

Table 3. Comparison of experimental and calculated diffusivities

Swelling agent	No. of runs	Experimental temperature range (°C)	Mean deviation $(D_{calc}-D_{obs})/D_{obs}$
Ethyl salicylate	13	106–128	−4.7%
1-Methylnaphthalene	10	106–124	−8.2%
Tetradecane	13	121–142	+4.6%

results therefore suggest slightly lower values than stated. It is noted also that the data in the *Handbook of Chemistry and Physics* are compiled from original 19th century references whose accuracy may be less than that of more recent measurements. Another compilation [18] presents results from a 1923 German source that are only very slightly lower than the older data.

Composite vapour pressure data for tetradecane are given for the range $133–1.013\times10^5\ \mathrm{N\,m^{-2}}$ (1–760 mmHg) [17, 18] but the actual measured range is not apparent. More recently, Rossini and Camin [19] have reported very precise data over the range 154–254°C and established the normal boiling point as 253.5°C. The only published lower temperature data are from the Thermodynamic Research Centre [20], whose figures are interpolated from the equation

$$P/\mathrm{N\,m^{-2}} = 133.3(P/\mathrm{mmHg});$$
$$\log P/\mathrm{mmHg} = 7.8179 - \frac{2236.75}{T-66.88}. \tag{2}$$

It is significant that this equation slightly underestimates the boiling point, suggesting that it is derived from rather lower temperature measurements. The actual measured range is again not stated but it was nevertheless hitherto regarded as the most reliable data at 20°C. The disparity between different estimates of the vapour pressure at 20°C in Table 4 exemplifies the uncertainty in long extrapolation of vapour pressure curves.

The position is very similar for n-dodecane, for which data are given for the range $133–1.013\times10^5\ \mathrm{N\,m^{-2}}$ (1–760 mmHg) [17, 18], but the more precise data of Rossini and co-workers [21] cover the range 126–217°C. Results obtained by interpolation in the Thermodynamic Research Centre's equation [20]

$$P/\mathrm{N\,m^{-2}} = 133.3P/\mathrm{mmHg};$$
$$\log P/\mathrm{mmHg} = 7.6685 - \frac{2023.90}{T-61.10} \tag{3}$$

are intermediate between extrapolations of the above at ca. 20°C; results from this source are again believed to be the most reliable at lower temperatures.

Of the compounds considered in this paper, only for 1-methylnaphthalene are there recently published results at ambient temperature obtained by a conventional method. Macknick and Prausnitz [22] measured the vapour pressure in the range 6–39°C and derived the equation

$$P/\mathrm{N\,m^{-2}} = 133.3P/\mathrm{mmHg};$$
$$\ln P/\mathrm{mmHg} = 20.552 - 6933.2/T. \tag{4}$$

Rossini and Camin [19] have reported very precise results over the range 142–245°C but their Antoine equation extrapolation predicts somewhat lower pressures at ca. 20°C than reported by Macknick and

Table 4. Vapour pressure of n-tetradecane at 20°C

P ($\mathrm{N\,m^{-2}}$)	P (mmHg)	Ref.
17.7	1.33×10^{-1}	17, 18
7.48	5.61×10^{-2}	19
11.4	8.56×10^{-2}	20

Prausnitz. Equation (4) significantly underestimates the normal boiling point but must be considered more reliable at low temperatures than a long extrapolation. The present work seeks to verify this.

EXPERIMENTAL

The method used was the weight-loss effusion technique originally described by Knudsen [23], the principle of which is that the rate of effusion of a vapour through a small orifice into a vacuum is proportional to its pressure. Provided that the orifice is sufficiently small that equilibrium is attained between a sample and its vapour, a substance in a container with a small circular aperture in the lid will lose weight at a rate proportional to its vapour pressure. It can be shown [24] from the kinetic theory of gases that, provided that the mean free path of the vapour is large relative to the dimensions of the aperture, the pressure is given by the relation

$$P = \frac{0.2285G}{KA_a}\sqrt{\frac{T}{M}}. \tag{5}$$

The apparatus comprises a cylindrical vacuum chamber surrounded by a jacket through which is circulated either water from an external thermostat bath or refluxing solvent vapour from an electrically heated reservoir below the jacket. A small sample pan with a tightly fitting lid is suspended in the vacuum chamber by means of a fine helical steel spring so that weight loss may be measured by observing the movement of the pan as the spring contracts. A thermocouple pocket enables the temperature to be measured within the chamber at a point close to the pan; the thermocouple indicates the temperature of the sample except insofar as it may be reduced by vaporisation but at the vapour pressures measured this effect is considered small relative to the temperature variation experienced (± 0.1 K). The whole jacket is lagged to ensure temperature uniformity. A vacuum of $< 1.3 \times 10^{-3}$ N m^{-2} ($< 10^{-5}$ mmHg) is obtained by a mercury diffusion pump backed by a two-stage rotary pump and is measured on a McLeod gauge.

When the apparatus attained a satisfactory vacuum and temperature stability, the position of a pointer on the pan, relative to a fixed point within the chamber, was observed at intervals using a cathetometer, from which was calculated the rate of movement (in cm s^{-1}). Under the normal total load of pan and sample the extended length of the spring is ca. 52 cm and previous calibration with this load has shown the further extension to be linear with load, the ratio being 0.0734 ± 0.0015 g cm^{-1}. This factor is combined with the measured rate of pan movement to obtain G in equation (5). The usual decrease in extension, i.e. movement of the pan, during a single run was 0.5–1.5 cm and measurements were read to ± 0.001 cm.

MATERIALS

Ethyl salicylate (puriss grade, ex Koch Light) and n-dodecane (GP Reagent grade, ex British Drug Houses) were both $> 99\%$ pure.

n-Tetradecane (ex Sigma Chemical Co.) was ca. 99%.

1-Methylnaphthalene was obtained from Aldrich, ca. 97%, boiling point 240–243°C.

RESULTS

Measurements were made over the approximate temperature range 20–55°C (9–35°C for dodecane) and results are shown in Table 5. Vapour pressure data may be correlated very well over moderate temperature ranges using an Antoine equation

$$\log P = A - B/(t + C). \tag{6}$$

Data over a short range may, however, introduce a false curvature due to random variation, particularly at each end of the measured range. Not only would such an equation give rise to serious errors if extrapolated outside the measured range but the dP/dT would also be incorrect within that range. This problem was overcome by making the assumption that a continuous, smooth vapour pressure curve must exist between ambient and higher temperatures; thus, the overall curvature may be constrained by the addition to our experimental results of one or more points from the aforementioned high temperature measurements.

For tetradecane and dodecane this was done by interpolating in the equations obtained by Rossini and co-workers [19, 21] at two temperatures, 20 K apart, at the lower end of their measurement ranges, namely 150 and 170°C for tetradecane and 100 and 120°C for dodecane. For the latter, it was noted that, although slightly below the actual measured range (126–217°C), predictions at these temperatures from Rossini's and the Thermodynamic Research Centre's equations agree extremely well. Rossini and Camin's results were used similarly to obtain values at 140 and 160°C for 1-methylnaphthalene. The absence of comparable data of assured accuracy for ethyl salicylate, however, made it more desirable to use the normal boiling point (233.75°C). Values of the constants A, B and C were obtained by a regression technique and are shown in Table 6.

Over a short temperature range, vapour pressure data are better represented by the Clapeyron equation

$$\log P = A' - B'/T \tag{7}$$

which avoids the above curvature problem but which is, of course, unable to represent the slight actual curvature which is present in the $\log P$ vs $1/T$ plots of most substances. The experimental points alone were fitted by least squares to equation (7) to obtain values of A' and B', also shown in Table 6.

The values of the constants lie within the normally

Table 5. Vapour pressure results

Ethyl salicylate			1-Methylnaphthalene		
T (°C)	10^2P (mmHg)	10^2P ($\mathrm{N\,m^{-2}}$)	T (°C)	10^2P (mmHg)	10^2P ($\mathrm{N\,m^{-2}}$)
19.9	3.97	529	20.1	4.36	581
21.6	5.06	675	31.5	10.7	1430
31.5	10.5	1400	39.5	18.2	2430
39.0	20.0	2670	39.6	19.9	2650
48.9	36.4	4850	48.9	32.3	4310
55.7	52.2	6960	56.1	46.1	6150

Dodecane			Tetradecane		
T (°C)	10^2P (mmHg)	10^2P ($\mathrm{N\,m^{-2}}$)	T (°C)	10^2P (mmHg)	10^2P ($\mathrm{N\,m^{-2}}$)
9.5	3.55	473	17.2	0.692	92.3
12.6	4.72	629	39.2	5.16	688
14.6	5.96	795	39.9	5.53	737
16.4	6.69	892	40.0	5.92	789
19.4	9.84	1310	48.5	12.3	1640
20.9	10.90	1450	55.5	21.9	2920
21.0	10.70	1430			
24.0	13.9	1850			
26.3	18.3	2440			
31.2	26.1	3480			
32.0	24.8	3310			
34.3	27.4	3650			
35.2	32.2	4290			

expected ranges, except for the C constant of 1-methylnaphthalene, which is rather higher than for most organic compounds. The effect of fitting the Antoine equation to the experimental data plus the normal boiling point (244.7°C) is shown for comparison.

A comparison of vapour pressures calculated from equations (6) and (7) and the most appropriate literature equation is given in Table 7. It is apparent that, as would be expected, there is close agreement between equations (6) and (7) over the normal ambient temperature range, the maximum difference being ±2%. It is also apparent that, while the two sets of Antoine constants given in Table 6 for 1-methylnaphthalene are significantly different, the interpolated vapour pressures differ by only 1%. Comparison with equation (7) results (Table 7), however, suggests that the Antoine equation based on the experimental points plus boiling point is the truer correlation; the reason why this is so is not apparent, but it must be noted that the differences between these three correlations are all small in comparison to the experimental uncertainties.

Our results confirm the earlier suggestion that the vapour pressure of ethyl salicylate at 20–30°C is rather lower than found by Kapur and Macleod; indeed it is also lower than obtained by extrapolation of data in the *Handbook of Chemistry and Physics*, but as discussed previously we regarded this as potentially unreliable. We noted previously that the Thermodynamic Research Centre's equations were apparently based on lower temperature data than others and were thus hitherto the most appropriate equations for dodecane and tetradecane. Our results are ca. 10% and 5% greater, respectively. It is interesting to note that Jordan [18] lists a set of smoothed points at 80–215°C for dodecane plus a single point at 48°C which is significantly higher than predicted from the others. While these results are from an older source and are higher than any of the more recent results

Table 6. Constants for equations (6) and (7)

	A	B	C	A'	B'
Ethyl salicylate	8.3343	2663.14	254.50	8.8870	3005.49
Dodecane	7.0113	1698.81	191.64	9.9624	3218.86
Tetradecane	7.2772	1940.97	188.19	10.7020	3738.01
1-Methylnaphthalene	10.2839 8.7782*	4198.00 3179.10*	341.07 294.26*	8.1083	2768.69

* Based on experimental points plus boiling point.

Table 7. Comparison of vapour pressure (N m^{-2}) results

	Temperature (°C)	(6)	(7)	Literature
Ethyl salicylate	20	5.72	5.76	7.73 [16]
	30	12.5	12.5	16.7
Dodecane	20	12.9	12.8	11.8 [20]
	30	29.6	29.5	27.1
Tetradecane	20	1.20	1.19	1.14 [20]
	30	3.21	3.13	2.99
1-Methylnaphthalene	20	6.05	6.15	6.01 [22]
	30	12.5	12.6	13.1
1-Methylnaphthalene*	20	6.12		
	30	12.6		
1-Methylnaphthalene†	20	5.99		
	30	12.6		

* See note in Table 6.
† Calculated from equation (8).

[19, 20] it may nevertheless be significant that extrapolation from high to low temperature resulted in underestimation of the vapour pressure.

Our results for 1-methylnaphthalene agree with those of Macknick and Prausnitz [22] to within 4% at 20–30°C, the differences being less than the combined uncertainties. This work therefore confirms their results as represented by equation (4) and the vapour pressure of 1-methylnaphthalene may thus be determined at normal ambient temperatures by either that equation or equation (6) or (7) using the constants in Table 6.

It is notable that results from two very different methods, namely gas transpiration (22) and effusion manometry (this work) should agree so closely. As noted above, equation (4) significantly underestimates the normal boiling point and thus extrapolation outside the measured range is unreliable. We therefore suggest it is most advantageous to combine the two sets of results to provide a correlation over the range 6–56°C. By including the normal boiling point as above to prevent anomalous curvature, the following equation is obtained

$$P/\mathrm{N\,m^{-2}} = 133.3(P/\mathrm{mmHg});\qquad \log P/\mathrm{mmHg} = 8.2302 - \frac{2727.21}{T-8.42}. \tag{8}$$

Equation (8) is preferred as it is based on the two data sets and is valid over a wider range. Values of the vapour pressure of 1-methylnaphthalene at 20 and 30°C calculated from equation (8) are given in Table 7.

DISCUSSION AND CONCLUSIONS

When the results of the open-tube experiments are re-analysed using the new vapour pressure data, excellent agreement is obtained with five different swelling agents with a 50-fold vapour pressure range: some results are shown in Table 2. Correlations for open-tube mass transfer with fully developed velocity and concentration profiles [25, 26] predict mass transfer coefficients about 25% lower than reported here. However, when an empirical correction for short transferring sections is applied [27] agreement to within 10% is obtained. Given that no great care was taken in the design of the entrance section of the apparatus, such agreement is entirely satisfactory.

A satisfactory inter-swelling agent agreement is also found in packed-bed wall mass transfer experiments [1]. Further, a study of particle to gas mass transfer in packed beds using ethyl salicylate and dodecane makes two points, Fig. 1. First, the experimental data at high Re_p where measurement errors are smallest does agree with the literature correlation [28], which is itself applicable only at high Re_p when a constant term in a Sherwood number correlation [29] may be neglected. Given the ill-defined and irreproducible geometry of a frequently re-packed packed bed, the agreement is satisfactory. Secondly, at high Re_p, the use of the new dodecane vapour pressure data is

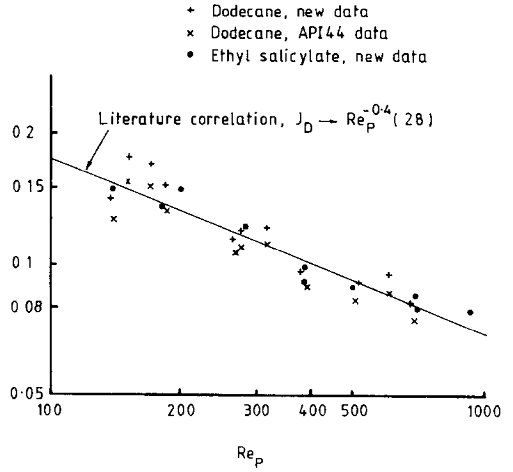

FIG. 1. j_D vs Re_p for particle to gas transfer in a packed bed ($d_o/d_p = 5.32$).

clearly justified, for the agreement with the ethyl salicylate data is obviously improved.

It is therefore concluded that:

(i) The new swelling agents identified here (hexadecane, tetradecane, 1-methylnaphthalene and dodecane) are suitable for use in the swollen polymer method. Improved vapour pressure correlations are provided.

(ii) The currently most widely used swelling agent, ethyl salicylate, is also suitable, but its vapour pressure is 25% lower than had been thought.

(iii) The simple open-tube mass transfer apparatus is very valuable. It can be used to measure the vapour pressure of potential new swelling agents by comparison with those already in use. Also, samples of swelling agent may be checked periodically for signs of degradation (indicated by an increase in vapour pressure) to which some, particularly esters, are susceptible.

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MESURE DU TRANSFERT MASSIQUE SOLIDE–GAZ PAR LA METHODE DU POLYMERE EXPANSE: ESSAIS D'AGENTS GONFLANTS

Résumé—On identifie un certain nombre d'agents gonflants qui sont des espèces migrantes, hexadecane, tetradecane, dodecane, 1-methylnaphtalène, pour l'utilisation par la méthode de Macleod du polymère expansé dans la mesure des taux de transfert massique solide–fluide. Les diffusivités dans l'air et leur pression de vapeur (sauf pour l'hexadecane) sont déterminées. L'agent le plus couramment utilisé est le salicylate d'éthyle; on montre que la valeur de sa pression de vapeur donnée dans la littérature (dans le domaine 20–40°C) est de 25% trop élevée. Après cette correction, on obtient des valeurs cohérentes du facteur *j* pour le transfert massique à la paroi d'un tube court, indépendant de l'agent d'expension utilisé.

MESSUNG DES FESTSTOFF–GAS-STOFFÜBERGANGS MIT DEM POLYMERQUELLVERFAHREN: UNTERSUCHUNG VON QUELLMITTELN

Zusammenfassung—Es werden einige neue Quellmittel, d.h. Übertragungsmedien zur Anwendung in Macleod's Polymerquellverfahren zur Messung des Feststoff–Fluid-Stoffübergangs nachgewiesen: Hexadekan, Tetradekan, Dodekan, 1-Methylnaphthalin. Die Diffusionskoeffizienten in Luft und die Dampfdrücke (gesichert für Hexadekan) werden bestimmt. Das früher am meisten angewandte Quellmittel war Äthylsalizylat, und es wird gezeigt, daß dessen Literaturwerte des Dampfdrucks (im Bereich 20–40°C) um 25% zu hoch sind. Nach dieser Korrektur werden konsistente *j*-Faktoren für den Stoffübergang von der Wand eines kurzen Rohres erhalten, unabhängig vom angewandten Quellmedium.

ИЗМЕРЕНИЕ ИНТЕНСИВНОСТИ МАССООБМЕНА МЕЖДУ ТВЕРДЫМ ТЕЛОМ И ГАЗОМ МЕТОДОМ МАКЛЕОДА. ОТБОР ИСПОЛЬЗУЕМЫХ ДОБАВОК

Аннотация—Рассмотрен ряд новых ускоряющих массоперенос полимерных добавок: гексадекан, тетрадекан, додекан и 1-метилнафталин, с целью их возможного использования для измерения скорости массообмена между твердым телом и жидкостью методом Маклеода. Определены коэффициенты диффузии этих добавок в воздухе и давление их паров (кроме гексадекана). Ранее в качестве такой добавки обычно использовался этилсалицилат. Показано, что приводимая для него в литературе величина давления пара (в диапазоне 20–40°C) завышена на 25%. С учетом этой поправки получены приемлемые *j*-коэффициенты массоотдачи стенки короткой трубы, значения которых не зависят от вида используемой добавки.