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The surface tension of tin-lead alloys in contact with fluxes

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As part of an experimental investigation of the capillarity and chemical basis of wetting and spreading as it applies to joining technology, the interfacial tensions between liquid lead–tin solder alloys and several gaseous and liquid fluxes have been measured by specially adapted classical techniques. Both an organic flux and liquid zinc chloride depress the interfacial tension over the full range of solder composition, the latter showing the more remarkable effect. The relevance of these measurements to the understanding of metal wetting and spreading behaviour is discussed.

1. Introduction

In the joining of metal components by soldering or brazing, a necessary condition is the wetting of the metallic substrate by the molten joining metal. In practice, the use of liquid fluxes is essential, their principal role being apparently the cleaning of both the substrate and solder by deoxidizing and degreasing. However, fluxes are also expected to have a strong effect on the surface tension of the liquid solder and, in common with other systems, one might expect a reduction in the solder surface tension. This should affect both the shape of the soldered joint and the spreading of the solder over the substrate.

The purpose of this work was to examine experimentally the contribution of the selected flux to the propensity of a solder to spread through its capillary action. Thus, considering that the flux achieves its maximum chemical cleaning effect and assuming that the flux does not influence significantly the surface free-energy of the solid substrate, the efficiency of spreading of the liquid metal over the substrate can be controlled through a reduced liquid metal–liquid flux interfacial tension. Measurements of interfacial tensions have been carried out for a range of lead–tin alloys, the basis of most common solders, and in the presence of gaseous "fluxes" (hydrogen or argon–hydrogen mixtures) or common liquid fluxes. Two separate classical techniques were adapted in order to conduct these measurements.

The results show that both of the representative liquid fluxes examined here reduce the surface tension of the liquid solder alloy below that in its own vapour or in the presence of hydrogen: hence, fluxes contribute to the spreading of solders through their effect on the surface tension.

2. Experimental procedure

2.1. Materials

The lead and tin base metals used in this work were of Johnson Matthey spectrographic purity and from these, alloys of known composition were produced by melting in a vacuum furnace. Two basically different liquid fluxes were selected with quite dissimilar chemical properties: (a) a non-corrosive synthetic organic flux and (b) zinc chloride. Both fluxes are commonly employed in practice.

The gaseous fluxes used here were hydrogen or argon–1 vol% hydrogen mixture. The hydrogen was purified by passing over a catalytic converter, then diffused through a palladium tube followed by drying in a column of molecular sieves. This resulted in a gas with a dew point of $-38°$ C. The argon–hydrogen mixture was obtained as a special high-purity gas which was subsequently passed through a column of molecular sieves for further drying.

2.2. Measurements of interfacial tension

The measurement of interfacial tension between

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the liquids as well as between the alloy and its vapour phase was carried out using two different and especially adapted techniques: (a) the sessile drop technique and (b) the maximum bubble pressure technique. These are reviewed in detail in [1]. Not only has each technique its individual advantages in certain regimes (which we shall discuss later), but the use of the two techniques effectively provides a check on the measurements.

2.2.1. Sessile drop (SD) measurements

This method is now well documented and only the features specially developed for this programme will be described here. The drop of alloy of known composition was located on a pyrex disc in a vertical furnace tube and, for measurements in a gaseous environment, the gas of known composition was established before the metal (which had been previously treated in hydrogen) was melted. For measurements at the liquid–liquid interface, the metal droplets were contained in separate cells together with the flux. In order to observe the profile of the liquid metal drop in contact with the gas or liquid flux at the temperature of the experiment, an X-ray shadowgraphing technique was used which provided sufficient contrast through differential X-ray absorption. This is demonstrated in Fig. 1, where in fact three specimens of different alloy compositions were mounted on top of each other, thus providing measurements simultaneously on samples under the same conditions. In turn, the calculation of the interfacial tension was carried out in the standard manner using the Bashforth and Adams [2] tables, the typical deviation of surface tension for any one condition being ± 6%. Further experimental details involving this technique are given in Appendix 1.

2.2.2. Maximum bubble pressure (MBP) technique

This is also a standard technique wherein a bubble of gas is blown through a bath of liquid under test and from the maximum pressure required to detach the bubble from an orifice of known size, the surface tension of the liquid in the presence of the gas composing the bubble can be calculated. The technique shown in Fig. 2 was adapted here so that by forcing a droplet of the liquid flux through the liquid solder, the interfacial tension between the metal and the flux might be measured. Further details of this adaptation of the technique together with the various drop detachment arrangements (Fig. 3) are given in Appendix 2.

3. Results and discussion

Interfacial tension measurements were made on the series of tin–lead alloys with compositions covering the full composition range, in two gaseous and two liquid fluxes.

As used here, the MBP technique is the more accurate (± 3%, see Appendix 2), however, for certain systems, the technique has serious limitations: thus, at 400° C the vapourization of organic flux may give rise to considerable error. This problem does not arise with the sessile drop technique where the samples are completely submerged in the liquid. For this reason, the measurements in the organic flux were carried out by the SD technique. Attempts to measure the interfacial tension in the zinc chloride flux with this method were not successful however, because the metal droplet spread over the pyrex substrate and measurement of the drop profile was not possible. This, of course, is a qualitative indication of a large effect on the interfacial tension.

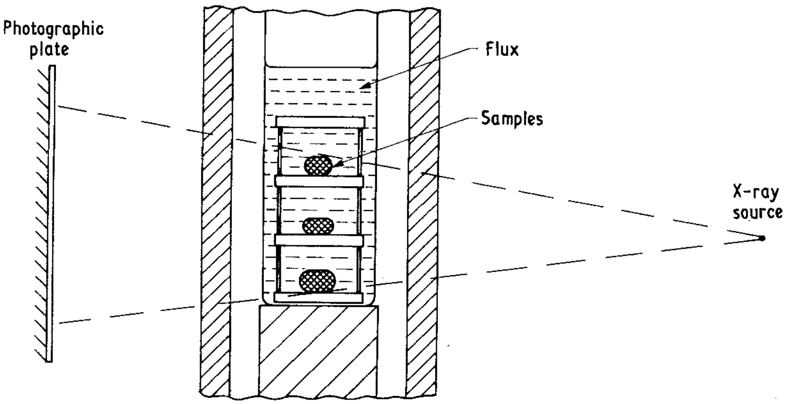

Figure 1 Sessile drop apparatus for measuring liquid metal–liquid flux interfacial tension by X-ray radiographic imaging of the drop profile. Three alloy compositions are studied here simultaneously.

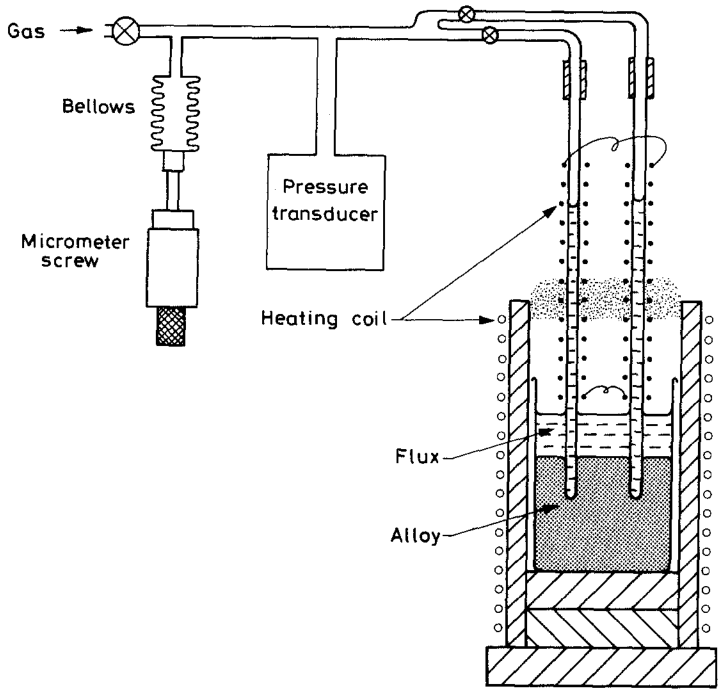

Figure 2 Maximum bubble pressure techniques for the measurement of liquid metal–liquid flux interfacial tensions.

Thus, because of the experimental constraints, only the MBP technique was used in the $ZnCl_2$ flux measurements; only the SD technique was used for the organic flux measurements, but both techniques were used in the gaseous environment measurements.

The surface–tension isotherm at 400° C in a hydrogen environment and across the complete Pb–Sn compositional range is shown in Fig. 4.

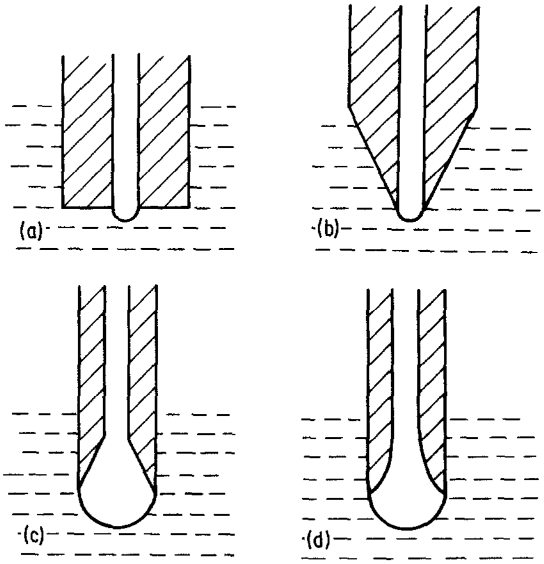

Figure 3 Schematic outlines for various capillary drop detachment nozzles.

Several of the plotted points represent values averaged over three independent measurements. The continuous curve is drawn through the values obtained by use of the MPB technique which, in this work, is inherently more accurate. However, the values obtained by the SD technique superimpose reasonably well on this curve when the ± 6% spread due to experimental error is taken into account.

The measurement techniques used here were adapted specifically for the determination of the liquid solder–liquid flux interfacial tension and because of the inherent experimental complexities, one might not expect these measurements to be as accurate as for the liquid–vapour surface tensions. Thus, the use of the X-ray shadowgraphic procedure to determine the outline of the sessile drop is intrinsically inferior to an optical procedure which permits a sharp focus on the drop perimeter. Since the two techniques can be used in the presence of a gas phase in contact with the liquid solder, such data were partly aimed at a check on the accuracy and self-consistency of the techniques by comparison with other published data.

The data obtained by the MBP technique are more accurate (± 3%) than those obtained by the SD technique (± 6%), however, both sets of data fit (within this scatter), the same continuous curve. Thus, we were not able to reproduce the data of Demeri *et al.* [3], who, for the same

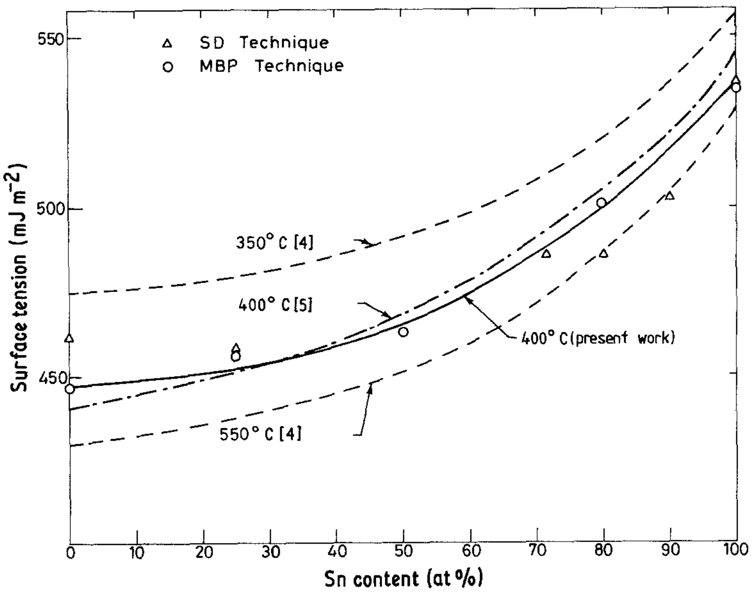

Fig. 4.

Figure 4 Surface tension of Pb–Sn alloys in hydrogen at 400° C: isotherm drawn through values obtained by MBP technique. Results compared with published isotherms at 350° C and 550° C [4] and at 400° C [5].

system and temperature reported a minimum in surface tension corresponding to the eutectic composition. This reported minimum was so pronounced, that it would have been observed by the present techniques. Apart from their use of a vacuum environment, the physico-chemical conditions appear identical. We cannot account for this difference in reported behaviour.

The present results, however, are consistent with the work of Hoar and Melford [4] who used an accurate capillary rise technique to determine surface tension isotherms for binary tin–lead alloys and who showed that the data were theoretically consistent with a modified form of the classical regular solution model which relates the surface tension of a binary mixture to the surface tensions of the pure components and the heat of mixing. Their data for 350° C and 550° C are indicated in Fig. 4 as dashed lines; note that here also, there is no minimum in surface tension. The present results for 400° C fall between the two sets of data and the change in surface tension with temperature is in the correct direction. More recently, Schwaneke *et al.* [5] have made extensive measurements in the present system at various temperatures. The broken curve shown in Fig. 4 is extracted from their data and refers to 400° C. This indicates a good agreement with the present results.

The above shows a consistency in measurements obtained by use of the present techniques, and this agreement on the same system and in identical physico-chemical conditions adds credibility to the comparisons on interfacial tension data obtained by application of the techniques separately.

The effects of a synthetic organic liquid flux "Xersin" and a zinc chloride flux on the surface tension of liquid solder are shown in Fig. 5, for alloys encompassing the full compositional range. It is seen that the organic flux depresses the surface tension significantly, while the $ZnCl_2$ flux induces a remarkable effect on surface tension.

The role of the organic flux in depressing the surface tension is very probably due to the adsorption of a component of the flux at the liquid–liquid interface. This particular commercial flux contains a halide and at the temperature of the measurements, some dissociation should be expected. Bondi [6] quotes a value of 455 $mJ\,m^{-2}$ for the interfacial tension between tin and "rosin" and a value of 389 $mJ\,m^{-2}$ for 65% tin solder in contact with "rosin". These odd values, which are the only data of this type we could find in the literature, are in broad agreement with the present data. The present results also fortify Bondi's speculative generalization that the interfacial tensions of liquid metals against organic substances are higher than those of liquid metals in contact with fused inorganic substances.

The interfacial tensions in the system $PbSn–ZnCl_2$ are remarkably low and give rise to high spreading coefficients. If, as has been suggested, Sn dissolves in the $ZnCl_2$, there would be a localized surface enrichment of Pb above the bulk level in

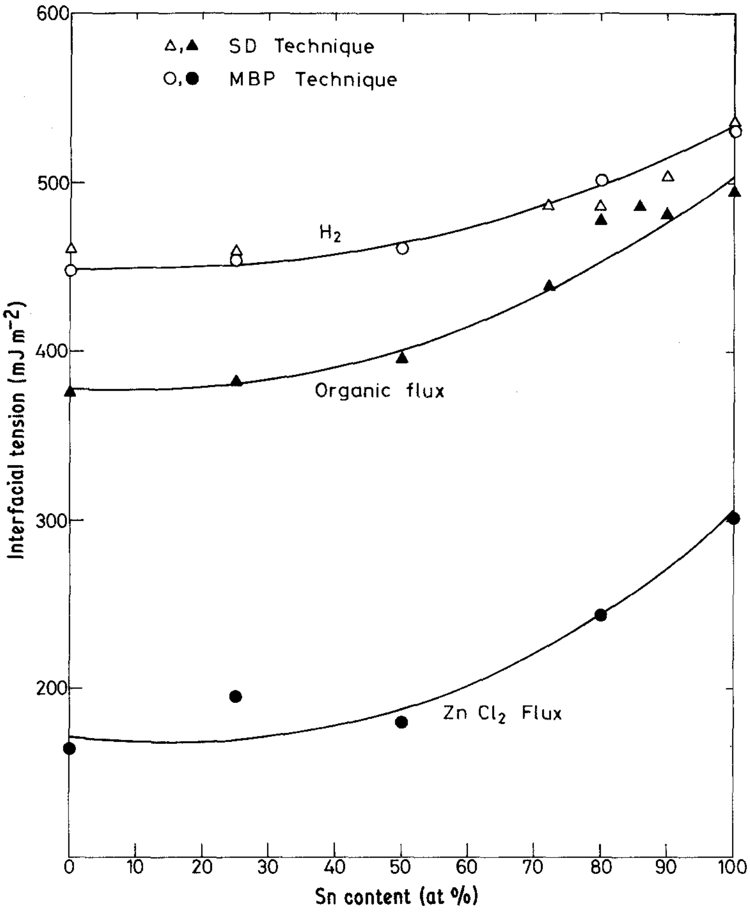

Figure 5 Effect of fluxes on interfacial tensions in liquid Pb–Sn alloys at 400° C: Values for the organic flux were obtained by the SD technique, for the $ZnCl_2$ flux, by the MBP technique.

the solder alloy although diffusion rates in the liquid state would militate against this. A surface enrichment of Pb would tend to reduce the interfacial tension; however, the measured effect is considerably greater than that which might be accounted for by this mechanism. A more plausible explanation is the polarization of the ions at the interface.

Speculatively, and in the absence of electrocapillarity data on the above systems, the surface activity of the fused salt is related to the polarizability of the metal ion and the above data for the $ZnCl_2$ electrolyte strongly support the idea of adsorbed salt molecules at the interface, probably with some degree of orientation. The evaluation of the amounts of interfacial excesses of the various ions would hence require knowledge of the electro-capillarity curve as a function of the chemical potential of the appropriate species and the application of the Gibbs Adsorption Theorem in Lippmann's analytical form.

For effective wetting of the substrate by the solder the contact angle, θ, should be zero in the simple equilibrium configuration shown in Fig. 6

$$_{S}\gamma_{L_1} = {}_{S}\gamma_{L_2} + {}_{L}\gamma_{L_2}\cos\theta, \qquad (1)$$

where γ is the interfacial tension and the subscripts S, L_1 and L_2 indicate the substrate, the liquid flux and the liquid solder, respectively. For zero contact angle, we are concerned with the spreading coefficient as the determinant of solderability, given by,

$$\Sigma = {}_{S}\gamma_{L_1} - {}_{S}\gamma_{L_2} - {}_{L_1}\gamma_{L_2}. \qquad (2)$$

Thus in practice, assuming that wetting takes place, a reduction in ${}_{L_1}\gamma_{L_2}$ will improve the spreading coefficient. The viscosity of the liquids will in turn determine the velocity of spreading. However, the effect of the flux on ${}_{S}\gamma_{L_1}$ or the substrate–flux interfacial tension is not clear and requires experimental investigation. For good spreadability, the role of the flux in capillarity terms should be to reduce ${}_{L_1}\gamma_{L_2}$, as we have seen, but not to diminish ${}_{S}\gamma_{L_1}$. From the chemical viewpoint, the flux should dissolve away surface oxides thereby allow-

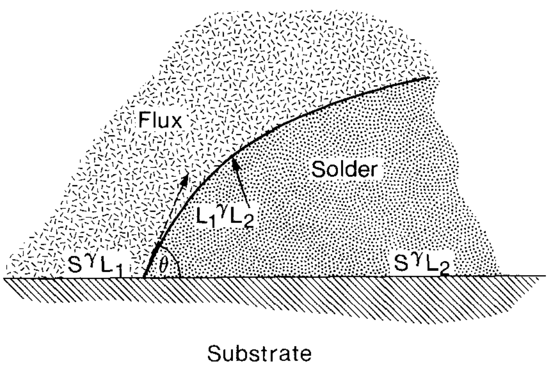

Figure 6 Schematic diagram showing the interfacial tensions involved in the wetting of the solid substrate by the liquid solder.

ing the zero contact angle to be maintained. One can speculate on a number of specific phenomena associated with fluxes: thus $ZnCl_2$ flux dissolves tin and by electrolytic action may deposit it on the substrate ahead of the spreading solder; this should not only keep the substrate clean, but ensure a substrate–flux interface with a high interfacial tension.

Appendix 1: Sessile drop procedure for liquid–liquid interfacial tension measurements (Fig. 1)

The samples of known alloy composition were placed in position and argon was passed for 6h while the furnace was gradually brought to temperature. The argon was replaced by hydrogen, and the temperature raised to 600° C, at which temperature the hydrogen flowed continuously until the emerging gas had the same (very low) dew point as the entry gas. This last condition could take up to 12h to attain. As required, the appropriate gas mixture was obtained and the temperature lowered to the working temperature at which the photographic exposure was made. Since the X-rays emanate from a small finite source, they are not parallel and thus provide a magnified image. This magnification was measured by replacing steel spheres in place of the samples and taking radiographs in totally simulated conditions, thus providing a complete calibration. The necessary dimensions on the shadowgraph were measured using an $X-Y$ travelling microscope. The sharpness of the image of the drop depends partly on the finite size of the source and partly on the exposure times, which could entail errors due to vibrations and the equipment. Exposure times with this equipment were up to 40 min. The equatorial diameter and height of each shadowgraphic image was measured separately 10 times, the typical spread ot the dimensions being ±2%.

Appendix 2: Maximum liquid bubble procedure for liquid–liquid interfacial tension measurements (Figs 2 and 3)

In this technique, the tips of the two capillary tubes of different radii were adjusted to the true horizontal position by raising a beaker of water on an adjustable platform until the surface touched both at the same time.

In the experiment, the bath of molten metal was brought up to the dry tips and an electric current passed through the heating coil around the tube. After cleaning the oxides from the surface of the liquid metal, the bath was raised so as to immerse the tips some 15 to 20 mm. Hydrogen was bubbled through rapidly for some 15 min, and then the gas flow rate reduced to about 2 bubbles per minute. The maximum pressure required to detach the bubbles was recorded for a series of up to 10 bubbles at a time. This was repeated by blowing the bubbles at a rate of one per minute. The depth of immersion was increased by 10 to 20 mm and the measurements repeated. This operation was repeated until the difference in the maximum bubble pressure between the two bubbles was constant.

The pressure was measured using an electrical transducer which gave a read-out of 1 mV for 1 mm of water pressure. This was a particularly useful device as the output was fed to two digital voltmeters which eased the problem of reading the maximum pressure. Thus for bubbling hydrogen into water, a typical pressure gave 40 mV with a spread of 0.05%, the spread being attributed to vibrations in the mountings.

A crucial factor for accuracy and reproducibility is the configuration of the capillary nozzle. For the simplest design, shown in Fig. 3a, the bubble forms at the sharp inner diameter; however, the slightest irregularity will cause the bubble to migrate away. Fig. 3b is an improved tip design and the bubble remains at the tip provided that it is very smooth. However, the slightest roughness, produced by the grinding finish may lead to the bubble moving up the outside cone, thus yielding a low value. Fig. 3c is an improved design, but the best configuration is that shown in Fig. 3d: by careful glass blowing and grinding, an internal cone was produced thus providing a gradual transition from the internal capillary bore to the outer tube diameter, from which the bubbles detached. The flame-polished tip was measured to better than ± 0.5% by a travelling microscope.

In order to measure the interfacial tension between metal and flux, the selected flux was added to the metal as a powder and allowed to melt to provide a depth of some 10 mm. The bath was next lowered until the tips were clear of the metal, but below the surface of the flux. In order to blow bubbles of flux through the liquid metal, the flux was first sucked into the heated tubes using a bellows, the bath was then raised until the tips of the tubes protruded into the metal, and the gas flow was used to force the flux out of each tube in turn while measuring the maximum pressure of each detached bubble. Calculations were made using the standard relationship

$$\Delta H \rho g = \Delta P = \left(\frac{1}{r_1} - \frac{1}{r_2}\right) 2\gamma, \quad \text{(A1)}$$

where γ is the interfacial tension, r_1 and r_2 the radii of the capillaries, ΔH is difference in manometer heights, here in units of centimetres of water, ρ is the density of water and ΔP is the difference in maximum pressure.

Among the sources of error, we note the density difference between the flux and the metal causes the bubbles to assume a non-spherical shape at the maximum pressure (but this can be corrected by Sugden's method [7]) also, the change in depth of immersion caused by the displacement of liquid must be kept small. Here, the difference in depth of the two tubes could be detected to an accuracy of ± 0.01 mm. Cumulatively, the error is expected to be less than ± 3%.

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References

1. E. D. HONDROS, in "Techniques of Metal Research, IV" Part 2, edited by R. A. Rapp (John Wiley and Sons, 1970) p. 293.
2. F. BASHFORTH and J. C. ADAMS, "An Attempt to Test the Theory of Capillary Action" (Cambridge University Press, London, 1883).
3. M. DEMERI, M. FARAG and J. HEASLEY, *J. Mater. Sci.* 9 (1974) 683.
4. T. P. HOAR and D. A. MELFORD, *Trans. Far. Soc.* **53** (1957) 315.
5. A. E. SCHWANEKE, W. L. FALKE and V R. MILLER, *J. Chem. Eng. Data* **23** (1978) 298.
6. A. BONDI, *Chem. Rev.* **52** (1953) 417.
7. S. SUGDEN, *J. Chem. Soc.* **121** (1922) 858.

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