The Wetting Behavior of Azeotropic Systems at Atmospheric and Reduced Pressures

Contact angles are reported for the azeotropic systems n-propanol-water and benzene-cyclohexane measured under distillation conditions at total reflux over a pressure range 50 to 760 torr on both copper and polytetrafluoroethylene surfaces. The influences of the solid surfaces, the surface tension positive and negative nature of the liquids, together with the changes accompanying the azeotropic shift with pressure on the wettability, have been established and shown to conform with wetting theory.

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SCOPE

The wettability of binary liquids which form azeotropes and whose surface tensions are strongly dependent on concentration have been determined for a range of pressures in a cell in which the contact angles can be measured at conditions which simulate total reflux in a distillation column. The object of the study was to establish if the wetting changes actually occurring were responsible for the large changes in efficiency of separation at concentrations near the azeotrope and at near-terminal compositions. No methods are available for predicting performance of columns in these regions and to date no interfacial properties have been reported for these conditions upon which the interfacial areas for transfer and so column efficiencies are dependent.

CONCLUSIONS AND SIGNIFICANCE

When aqueous mixtures of n-propanol are distilled below the azeotropic composition, representing a surface tension positive system (that is, where the lighter component has the lower surface tension on copper which is a surface with a high surface free energy), a reduction in pressure has been shown to cause a decrease in wettability. Conversely, for n-propanol concentrations above the azeotrope, which is a surface tension negative system, an increase in wetting resulted when the pressure was reduced. With the low energy surface polytetrafluoroethylene for any propanol composition, the wetting was found to be independent of pressure and temperature. For the benzene-cyclohexane system, however, the wetting behavior was not found to be analogous to that described when using n-propanol-water since an additional effect which was attributed to the cyclohexane being absorbed on the polytetrafluoroethylene surface was encountered.

The azeotropic shift caused by varying the pressure was shown to result in binary mixtures which have compositions close to the azeotrope, changing from surface tension positive to negative in nature with accompanying differences in wetting behavior. The dependency, wetting on concentration, in particular near the azeotrope and at near-terminal values predicted by considering the relative contributions played by the vapor-liquid, liquid-solid, and vapor-solid interfaces, was in accord with the experimental findings.

The data point conclusively to the controlling role played by wetting on column performance using these systems. They also illustrate that design of distillation columns for separation of azeotropic systems or dilute solutions which exhibit a marked dependency of surface tension with concentration cannot be successfully achieved unless these measurements are made.

For a pure liquid it is observed that wetting is promoted with increasing temperature because of a corresponding reduction in surface tension. When a binary liquid is considered, the interchange of components between the liquid and vapor may produce a higher or lower surface tension, and this will increase or decrease the wetting. This influence has been studied by Zuiderweg and Harmens (1958) who defined three types of systems with respect to surface tension changes—positive, negative, and neutral—and designated systems as positive when the less volatile component of the binary mixture had the higher surface tension and negative when this component had the lower surface tension. The term neutral was given to those systems in which either the components do not show a difference in surface tension or in which the relative volatilities are very low and the gradients in surface tension are consequently small. Systems that demonstrate azeotropic behavior exhibit both surface tension positive and surface

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tension negative tendencies since the azeotrope, which is the more volatile component, has a higher surface tension than one of the pure components and a lower surface tension than the other, as illustrated in Figures 1 and 2 for the systems n-propanol-water and benzene-cyclohexane at their boiling points.

For systems showing no azeotropic behavior Boyes and Ponter (1970a) have assessed wetting properties by the measurement of contact angles for both surface tension positive and negative mixtures. It was shown (Boyes and Ponter, 1971) that for a surface tension positive system exhibiting no interfacial turbulence at the vapor-liquid interface the wetting was directly related to the efficiencies obtained in packed columns. For the surface tension negative systems, higher efficiencies were obtained than one would have predicted by considering the changes in surface area which would occur on the film-contacting device. It was observed (Boyes and Ponter, 1970b) that the large interfacial turbulence which accompanied transfer using these systems was sufficient to cause ejection of liquid droplets into the vapor phase, so overcompensating for the loss in area occurring because of film rupture.

Little data have been reported on the wetting changes accompanying azeotropic distillation. Qualitative assessments have been referred to in the literature based on visual inspection where ropes of liquid have been observed when distilling azeotropic mixtures in glass columns. A more quantitative evaluation was made by Norman and Binns (1960) when investigating the Minimum Wetting Rates (M.W.R.) to maintain a complete film of liquid on a glass wetted-wall distillation column using n-propanol-water mixtures. The M.W.R. for pure water in equilibrium with its vapor was 12 lb/hr. ft. but with 5% of propanol the M.W.R. was reduced to about 1 lb/hr. ft. owing to the increase in surface tension as the liquid flowed down the column. As the propanol content approached the azeotropic composition (43 mole % propanol) the M.W.R. rose sharply; this rise was continued above the azeotropic composition. High wetting rates were needed in the region where the propanol is transferred from the vapor to the liquid, and when the mixture contained between 70% and 80% of propanol the M.W.R. was so high that it was impossible to maintain a continuous film. The results were correlated empirically using a $\Delta\sigma$ term (that is, the difference in surface tensions corresponding to the liquid in equilibrium with the vapor and the average film composition). No consideration was paid to the influence of the nature of the solid surface in this investigation.

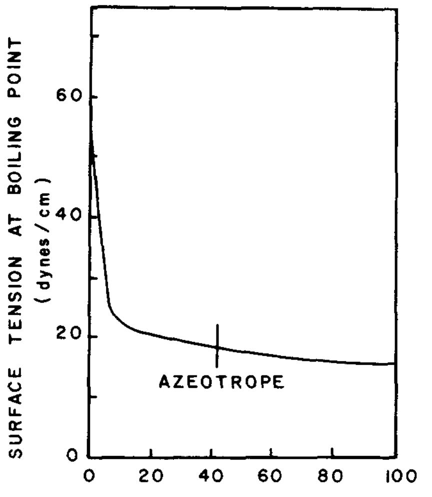

Fig. 1. Surface tension of n-propanol-water mixtures at their boiling point.

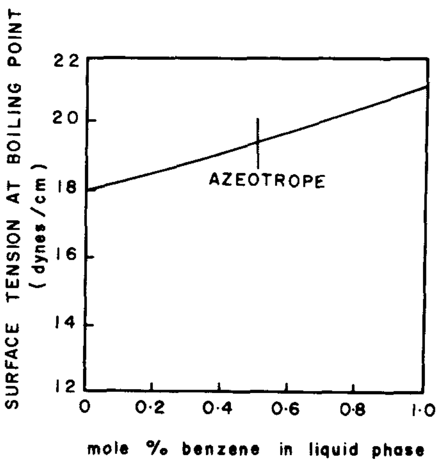

Fig. 2. Surface tension of benzene-cyclohexane mixtures at their boiling point.

The following investigation of two azeotropic binary mixtures—one aqueous in nature—for a range of pressures up to one atmosphere was carried out to assess the wetting characteristics, upon which the wetted area of the packing and hence the performance of a packed distillation column is dependent. Two different solid surfaces representing a large variation in surface energy were selected. They were copper and polytetrafluoroethylene, the former having a high value similar to materials of normal industrial usage, such as stainless steel, porcelain, glass, etc.

EXPERIMENT

The copper specimens used in the experiments were 99.99% pure and were prepared in the following manner. A flat plate 2.54 cm. in diameter and 0.7 cm. thick was polished with numbers 220, 330, 400, and 600 silicon carbide paper and then on a wheel using 'Buehler A B Microcloths' impregnated with 6 micron diamond paste. The specimen was then degreased with a mild soap solution and washed with distilled water, absolute ethyl alcohol, distilled water again, and finally in the test liquid. The polytetrafluoroethylene specimens 2.54-cm. sq. by 0.6 cm. thick were prepared by polishing with 600 carbide paper followed by polishing on a wheel using silk cloths and 5, 0.3, and 0.05 micron Alumina polishing compound. (The cleaning technique was the same as described above for the copper specimens.) Since a possibility of Alumina particles embedding in the surface of the polytetrafluoroethylene [Ellison et al., (1967)] existed, the samples were examined for particles of alumina with a Multiple Attenuation Total Reflection technique, with samples polished with the alumina compound and untreated samples. No such particles were detected. The surface roughness (center line average) of the specimens, 1.0 micro in. for copper and 0.4 micro in. for polytetrafluoroethylene, was measured using a Talysurf meter employing the standard techniques. The results are averages of at least 15 readings. The specimens were prepared as described before each run.

The glassware was washed with absolute ethanol to remove excess grease and then cleaned with a sodium dichromate-sulphuric acid solution before being irrigated several times with distilled water and finally with the liquid under use.

The water used in the experiments was triple distilled, each stage incorporated a surface overflow section which continuously removed surface contaminants. Using a Du Nouy Ring Balance the final product was shown to have a surface tension of 72.8 dynes/cm. at 20°C. which is in excellent agreement with reported values.

As the experiments were carried out over a range of pressures, a Cartesian manostat was selected as a pressure control above all others since it was suitable for the pressure range investigated.

All septums used on the apparatus and rubber stoppers used on the manostat were repeatedly boiled in the test liquids which showed no change in surface tension at the end of the operation. All joints on the apparatus were fitted with Teflon sleeves to eliminate contamination from conventional sealants. The 'Speedivac' high vacuum oil pump used for the low pressure work was situated some 6 meters from the apparatus and had an ice-acetone vapor trap in the glass line between the pump and the apparatus to eliminate any oil contamination in the vapor phase and also to protect the pump. The contact angles were measured under conditions simulating distillation at total reflux using the apparatus illustrated in Figure 3. Essentially the apparatus consisted of a one-liter flask, a glass wetted wall column 6 cm. in diameter and 30.5 cm. in length, and a C 5/12 "Quickfit" condenser. The column was fitted with two optical flats placed on opposite sides of this section. Transmitted light was used from the back of the cell to the travelling microscope. This method was found to give the best image of the point of contact of the liquid, solid, and vapor. The one-liter flask was fitted with a thermometer pocket and was heated by means of a 450 watt isomantle fitted with a control. Stainless steel wire gauze was added to the contents of the flask to prevent bumping. The vapor was condensed in a water cooled condenser and refluxed as a film down the column. A liquid sampling device was fitted to the column wall directly opposite the sample plate. The column was fitted with an isotope controlled by a Variac. Both the column and the flask were lagged with asbestos rope to reduce heat losses.

The apparatus was assembled as shown in Figure 3, and the overflow device at the top of the column was ensured to be horizontal by lining up one of the cross wires in the telescope with a thin plumb line, rotating the goniometer eyepiece through 90°, and then lining up the cross wire with the surface of the overflow device. Then the apparatus was clamped in position. The top section of the column was removed leaving the glass table exposed. A spirit level was placed on the glass table and the table held by a clamp. With a glass blowers' torch the glass stem was heated to allow movement of the table. The table was then set horizontally and held in this position until the glass stem cooled. Once set in this manner, the glass table was always parallel to the overflow device at the top of the column. Thus when the column was reassembled after cleaning, the above method ensured that only the table had to be aligned by simply using a spirit level. When this was done, the overflow device was horizontal when the column was put in place. This procedure ensured that an even distribution of liquid flowed down the column wall and that the plate was horizontal. After the leveling procedure the sample plate prepared as described previously was introduced into the equipment and the apparatus assembled.

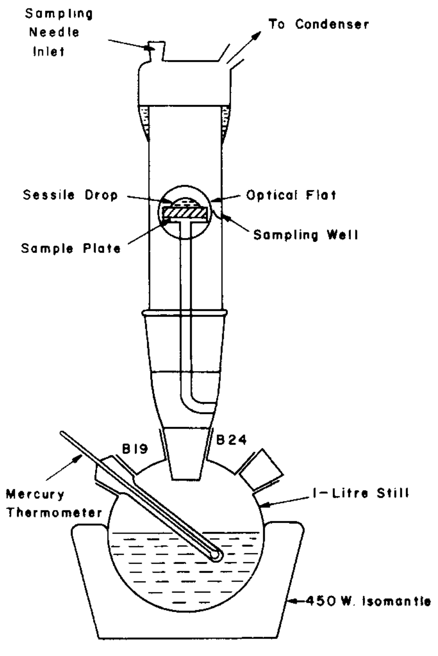

Fig. 3. Diagram of apparatus employed for contact angle measurement under total reflux conditions.

At the start of each run the contents of the flask were brought to the boil and the heat input controlled to give the desired boil up rate. When steady state was reached (after approximately 2 to 3 hours), a liquid sample was withdrawn from the sampling well in the wall of the column and was transferred directly and injected carefully onto the copper plate by a 10 ml. 'Plastipak' sterile disposable syringe fitted with a stainless steel needle approximately 27 cm. in length. The needle had been previously introduced utilizing the inlet provided at the top of the column and covered with a septum. The contact angle was measured immediately with the travelling microscope. This procedure was repeated at least five times and the reported contact angle, an average of these readings has standard deviations in the range 0.5 to 1.0 degree. At the end of each run, a liquid sample was taken from the column by the syringe and analyzed with a refractometer maintained at 20°C ± 0.1°.

The experimental contact angle-concentration data for the binary systems n-propanol-water and benzene-cyclohexane obtained on copper and polytetrafluoroethylene surface of specified roughness for the pressure range 50-760 torr. are presented in Figures 4 to 7.

DISCUSSION

It is advantageous to examine the wetting behavior of the liquid mixtures on the copper and polytetrafluoroethylene surfaces separately. For the n-propanol-water system it is evident at low compositions and compositions near the azeotrope that large changes in wetting accompany small variations in concentration using the copper surface. It is also apparent that the behavior is markedly influenced by changes in pressure. With the polytetrafluoroethylene, it can be seen that at a given concentration the wetting is not affected by pressure except to a small degree near the azeotropic composition and that no variation in wetting is observed at the near-terminal composition. An explanation of these phenomena is afforded by considering a sessile drop of liquid on a solid surface at equilibrium and resolving the forces at the three-phase boundary.

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} \tag{1}$$

By differentiating with respect to ln c,

$$\cos\theta \frac{d\gamma_{LV}}{d(\ln c)} - \gamma_{LV} \sin\theta \frac{d\theta}{d(\ln c)} = \frac{d\gamma_{SL}}{d(\ln c)} - \frac{d\gamma_{SL}}{d(\ln c)} \tag{2}$$

results. Gibbs surface excess is given by

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d(\ln a)} \tag{3}$$

For dilute solutions the activity may be interchanged with the concentration.

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d(\ln c)} \tag{4}$$

Similarly, the same interchange may be made for conditions close to the azeotrope since an azeotrope exhibits the same thermodynamic characteristics as a pure substance (Rowlinson, 1969). Thus the logarithm of the azeotropic pressure is a linear function of $1/T$. Combining Equations (2) and (4) gives

$$\gamma_{LV} \sin\theta \frac{d\theta}{d(\ln c)} = RT\,(\Gamma_{SV} - \Gamma_{SL} - \Gamma_{LV}\cos\theta) \qquad (5)$$

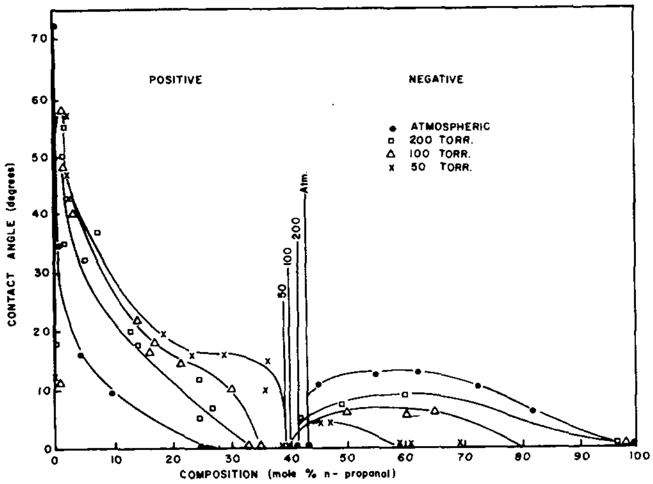

Fig. 4. Contact angles measured under conditions simulating distillation at total reflux for the system n-propanol-water on a copper surface over a range of pressures 50 to 760 torr.

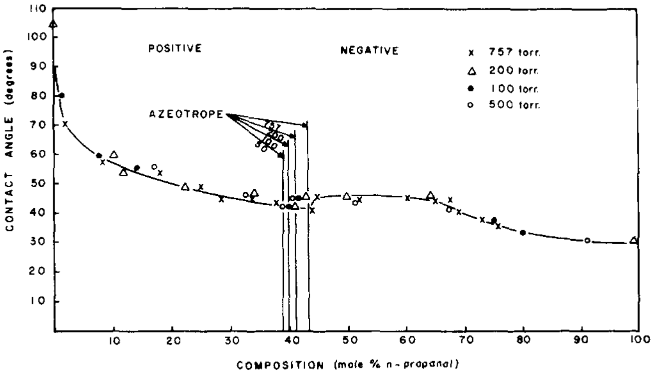

Fig. 5. Contact angles measured under conditions simulating distillation at total reflux for the system n-propanol-water on a polytetrafluoroethylene surface over a range of pressures 50 to 757 torr.

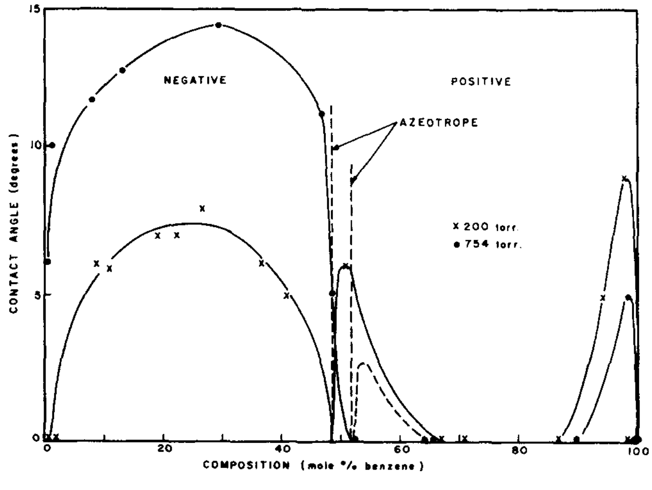

Fig. 6. Contact angles measured under conditions simulating distillation at total reflux for the system benzene-cyclohexane on a copper surface at atmospheric pressure and 200 torr.

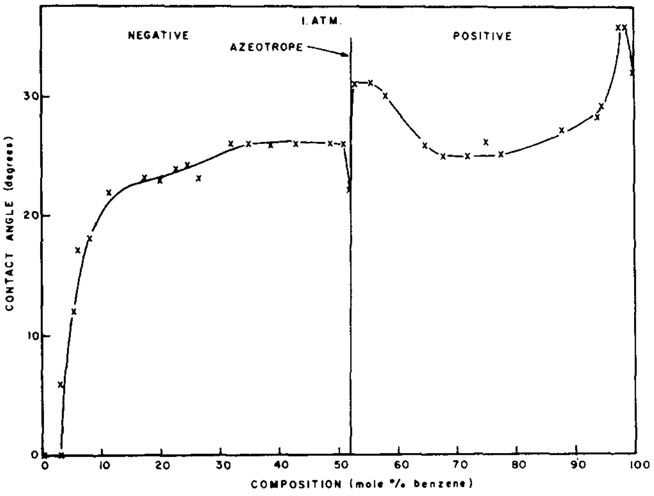

Fig. 7. Contact angles measured under conditions simulating distillation at total reflux for the system benzene-cyclohexane on a polytetrafluoroethylene surface at atmospheric pressure.

For the copper surface where adsorption of vapor onto the solid surface gives a positive Γ_{SV} component, the initial decrease in wetting with an increase in concentration is followed by a levelling and final increase as the value of Γ_{SV} is equaled and then overtaken by the combined ($\Gamma_{SL} + \Gamma_{LV}\cos\theta$) component. In the case of the polytetrafluoroethylene, there is no adsorption of vapor on the surface and the right-hand side of Equation (5) always takes the same sign resulting in no behavioral inflexion. Superficially it would appear that the behavior on the copper surface at one atmosphere is anomalous as no maximum is observed in Figure 4. However, it would appear likely that this point occurs at a lower concentration than investigated, that is, below 1 mole %, since the maxima in the curves occurs at decreasing concentrations as the pressure increases.

For the benzene-cyclohexane system similar behavior is observed with the copper surface as previously described using n-propanol-water mixtures. However, when using polytetrafluoroethylene this time, maxima are again exhibited at low concentrations and for conditions close to the azeotropic point. It has been demonstrated by Whalen and Wade (1967) that no adsorption of vapor on the polytetrafluoroethylene will occur. However, Graham (1965) has demonstrated that cyclohexane is absorbed, so introducing a Γ_{SV} term into Equation (5).

Dividing the two binary systems into their surface tension positive and negative regimes—for the copper surface, the positive systems, that is, n-propanol-water (below the azeotrope) and benzene-cyclohexane (above the azeotrope)—the contact angles increased with a decrease in pressure. At the same time the contact angles decreased with decreasing pressure in the negative regions as demonstrated in Figures 8 to 10.

This behavior may be explained again by considering Equation (1). For a given liquid concentration in the positive region, a reduction in pressure (with its accompanying decrease in temperature) will produce an increase in γ_{LV}. γ_{SL} will increase slightly and γ_{SV} will be reduced since at lower pressures more of the lighter component will exist in the vapor phase, resulting in an increase of the more volatile component adsorbed on the solid surface. So from Equation (1) $\cos\theta$ will decrease, that is, an increase in contact angle will occur. For the negative region

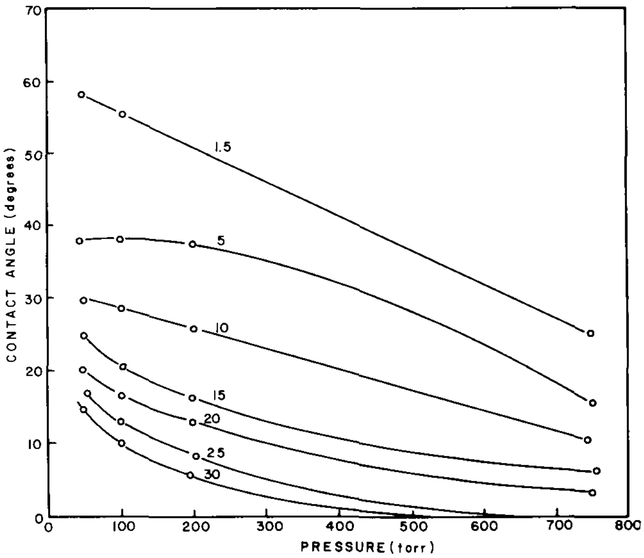

Fig. 8. Contact angle versus pressure for the positive system (n-propanol-water below the azeotrope) for given mole % concentrations of n-propanol on a copper surface.

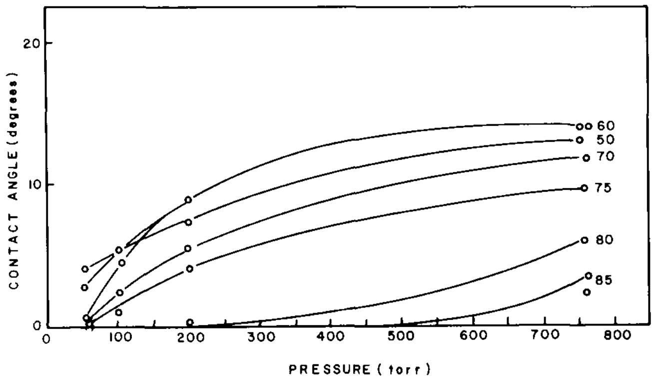

Fig. 9. Contact angle versus pressure for the negative system (n-propanol-water above the azeotrope) for given mole % concentration of n-propanol on a copper surface.

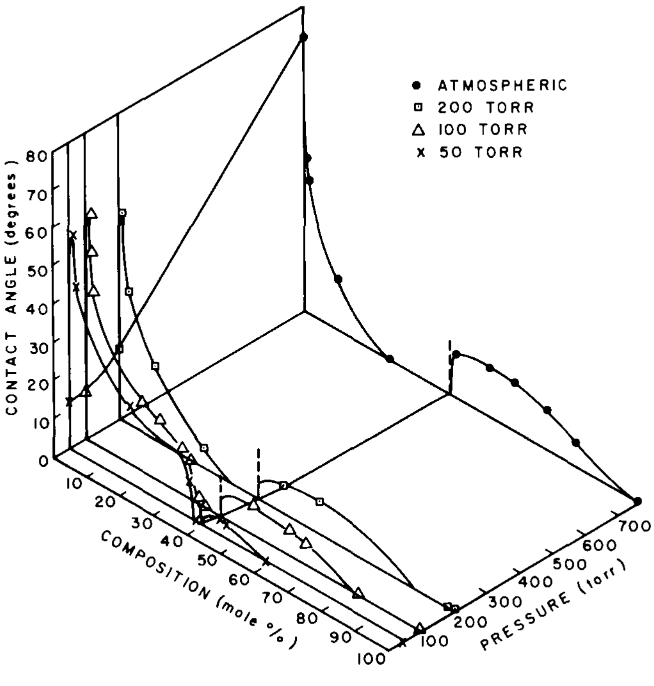

Fig. 10. Contact angle versus composition for a range of pressures 50 to 760 torr for the system n-propanol-water on a copper surface.

the more volatile component will have the larger surface tension, increasing the value of γ_{SV} and so producing a decrease in the angle with reducing pressure.

The data for the copper surface demonstrate the importance of wetting properties in assessing the variation of distillation efficiencies using film contacting devices with pressure. From these studies it would be expected that for systems where the surface properties are controlling, a decrease in pressure would result in a decrease in efficiency for a surface tension positive system and an increase in efficiency for a surface tension negative system.

Using the polytetrafluoroethylene surface for the system n-propanol-water, invariance of contact angle was demonstrated with pressure. In a separate experiment, contact angles were measured using the same systems at room temperature in the presence of argon saturated with its vapor. These are plotted with the contact angles obtained under distillation conditions in Figure 11. The difference in behavior can be attributed to the effect of mass transfer alone, as it has been already demonstrated the pressure and temperature have no effect on contact angle on a polytetrafluoroethylene surface (Ponter and Boyes, 1971). For the system benzene-cyclohexane (Figure 7) and for the surface tension positive section (above the azeotrope), a maximum contact angle is obtained in the low cyclohexane composition region. This behavior is explained again in terms of the afore-described absorption process.

Of practical importance when considering the effect of pressure on the wettability of azeotropic systems is the variation of the azeotropic composition with pressure.

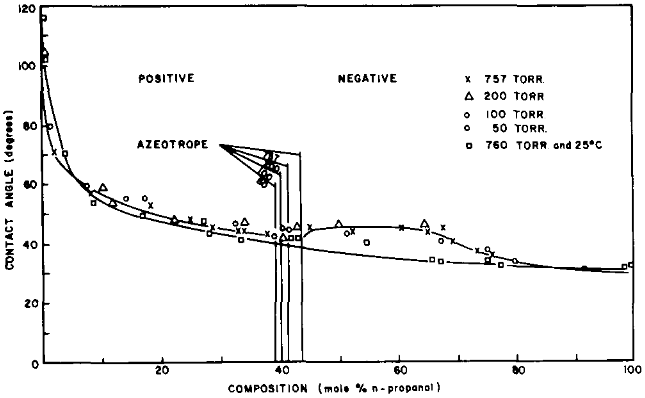

Fig. 11. Comparison of contact angles measured under distillation conditions and equilibrium conditions (at 25°C. and 1 atm.) for the system n-propanol-water on a polytetrafluoroethylene surface.

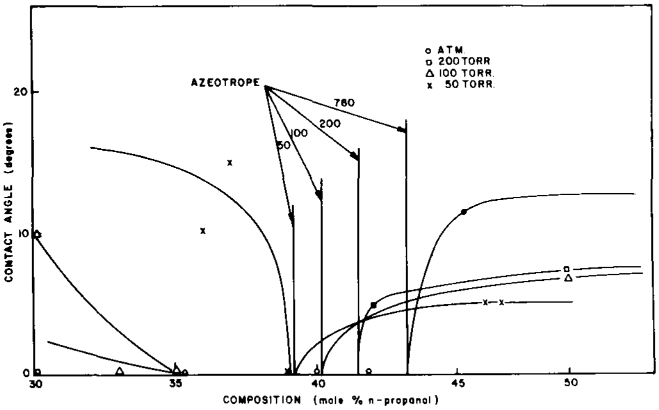

Fig. 12. Change in wettability due to the azeotropic shift with pressure for the system n-propanol-water on a copper surface.

Thus, for 42 mole % n-propanol, a change in pressure from 760 to 200 torr will result in the system changing from surface tension positive to negative because of the azeotropic shift. This phenomenon, illustrated with both systems and solid surfaces in Figures 12 to 15, can be explained by considering that for a change in pressure there are corresponding changes in the surface nature of the system and the surface excess, resulting in an excess of alcohol to an excess of water, so increasing the surface tension and producing an increase in contact angle. This effect is separate from that of temperature since for the n-propanol-water system on a polytetrafluoroethylene surface, the effect of pressure and temperature is negligible. Therefore, the wetting behavior produced over the concentration range 39.2 mole % to 43.2 mole % n-propanol is caused by the change from a positive to negative system. For the n-propanol-water system on a copper surface, the increase in contact angle produced by the azeotropic shift is to an extent counteracted by the reduction in pressure which as shown previously reduces the contact angle for a negative system.

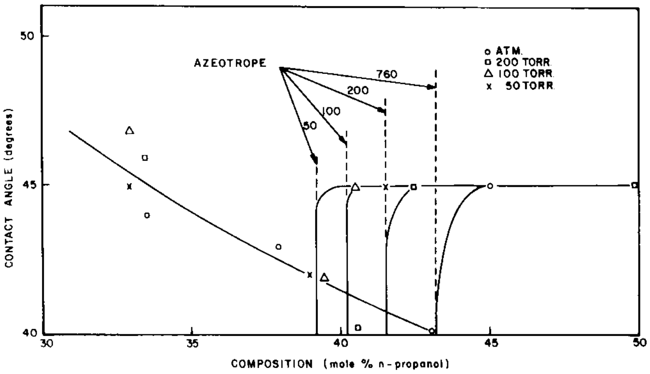

Fig. 13. Change in wettability due to the azeotropic shift with pressure for the system n-propanol-water on a polytetrafluoroethylene surface.

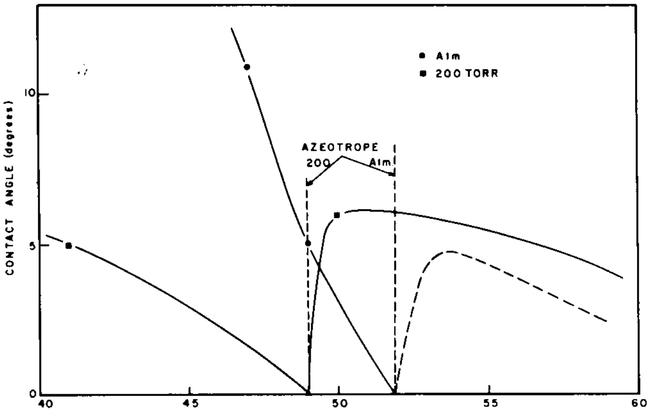

Fig. 14. Change in wettability due to the azeotropic shift with pressure for the system benzene-cyclohexane on a copper surface.

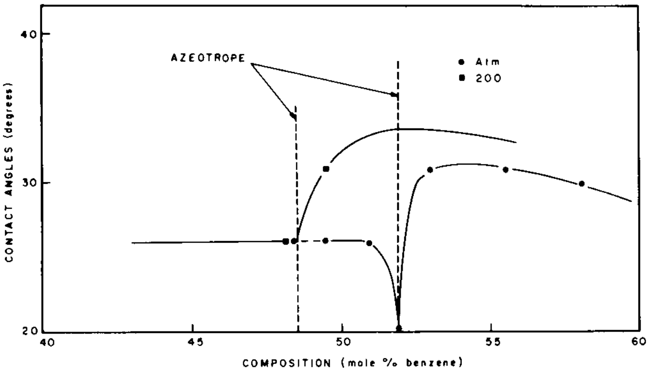

Fig. 15. Change in wettability due to the azeotropic shift with pressure for the system benzene-cyclohexane on a polytetrafluoroethylene surface.

This observation is important because surface wetting under mass transfer conditions can change, depending on whether the more volatile component is being positively or negatively absorbed at the liquid-vapor interface. This explains the behavior, say, of a methanol-water system which under distillation conditions is positive and stable; however, if an aqueous pendant water drop is suspended in an environment of methyl alcohol vapor, the drop will be unstable.

ACKNOWLEDGMENT

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NOTATION

c = concentration of more volatile component
R = gas constant
T = temperature

Greek Letters

γ = interfacial free energy
Γ = surface excess of the more volatile component per unit area
θ = contact angle

Subscripts

LV = liquid-vapor
SL = solid-liquid
SV = solid-vapor

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