# Surface Tension Considerations for Membrane Casting Systems

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## Synopsis

Surface energy considerations in the context of membrane preparation are examined. The viability of a membrane-casting system can be successfully assessed with pertinent surface tension data. It is illustrated how surface tension data for multicomponent casting solutions can be used to resolve the surface structure of asymmetric reverse osmosis membranes.

## INTRODUCTION

Surface chemical phenomena associated with polymer solutions used for the casting of asymmetric membranes are examined in this paper. Laboratory research was conducted to establish surface tension measurements on polymer solutions as a viable means to determine the suitability of additives, polymers, and/or their solutions in organic solvents to be used for casting asymmetric phase inversion membranes. It was first suggested by Tanny[1] that the surface tension behavior may be used to elucidate the extent to which the equilibrium and dynamic parameters play a role in asymmetric structure formation.

As background to the topic, the following is a brief description of how membranes are produced: A polymer solution, generally with additives, is spread in a very thin layer (i.e. with a doctor blade) over some support or backing material. The layer is left exposed to the air for a short time (the holding period), and then immersed into a gelation bath. The gelation bath, usually water, is miscible with the organic solvent in the polymer solution but precipitates the polymer into a solid porous film. The pores result from water displacing solvent and/or additive held within the polymer as it solidifies. A network of pores through the membrane is formed by the held solvent diffusing into the gelation bath and its subsequent replacement by the bulk liquid in the bath. Hence, it can be seen that the physicochemical nature of the membrane-casting system ultimately determines whether the membrane will be of any practical use, but within this framework, surface phenomena and interfacial dynamics are the actual mechanisms by which the membrane's skin structure is established.

Polymers can be selected for use as separation membranes on the basis of their chemical nature with respect to a particular application. In this sense, cellulose acetate was one of the earliest polymers found to be an effective membrane material for the desalination of water due to its preferential sorption for water and/or preferential repulsion for aqueous salt solute.[2]

It was discovered that membranes formed by the phase inversion method are asymmetric in structure. The cross-section of a membrane can be divided into two distinct regions. Typically, the bulk of the membrane is quite porous while the layer adjacent to the gelation bath is denser and considerably less porous. The dense polymer layer or "skin" is necessary and responsible for separations.

There are two mechanisms whereby the polymer in the casting solution can be concentrated on the surface of the casting solution film. First, if the organic solvent is volatile and evaporates from the surface during the holding period at a faster rate than the polymer can diffuse back, causing a higher polymer concentration, and second, the surface tensions of polymers are not in excess of the solvents. These mechanisms are not well defined in the literature, as there is a probable dependence on the history of the interface. Thus due to a surfactancy effect, the polymer may equilibrate at the surface in a higher concentration than in the bulk of the solution. This can be viewed in a general sense, analogous to the effects in salt/water and surfactant/water systems where the presence of an additive results in a surface tension change. The surface tension which is a two-dimensional conceptualization of the state of matter, should not be confused with the cohesive energy density which is a three-dimensional materials property. Knowledge about which of these mechanisms hold in a particular casting solution will have a profound influence in subsequent membrane-casting steps.

It is thus apparent that surface tension data on polymer solutions is valuable for determining whether or not one would expect an asymmetric membrane to be formed for a given system upon casting. In a broader sense, such data would provide information on the surface composition of complex, multicomponent polymer solutions, and can be a guide to the choice of the individual components.

A primary objective of this research was to identify and clarify the role of surface phenomena in membrane-casting systems. Additionally, it was desired to establish criteria for the elucidation of surface properties of membranes by means of surface tension data on polymer solutions and solvent additive solutions.

## EXPERIMENTAL

The laboratory research conducted consisted primarily of a series of surface tension measurements on polymer solutions pertaining to membrane-casting systems. The effect of polymer concentration was examined by testing different strengths of selected solvent-polymer systems. The method of measuring the surface tension was the drop weight adapted for the systems of interest to membrane compositions given by Becher.[3] Solvent-solvent systems and some relevant ternary systems were also examined.

The solvents used in the polymer solutions included acetone, dimethyl acetamide (DMA), n-methyl pyrrolidinone (NMP), and dimethyl sulfoxide (DMSO). The solvents were supplied as reagent grade and were subsequently vacuum-distilled in an apparatus with greaseless joints prior to use.

The polymers, which included Eastman Kodak cellulose acetate E 400-25 (CA), polyamidehydrazide (8273) (PAH), and Udel P1700 polysulfone (PS), were commercially available types except for the PAH which was prepared
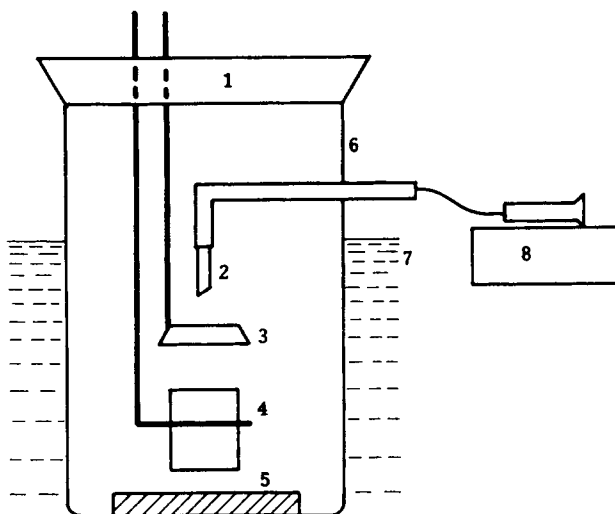
Fig. 1. Schematic diagram of the drop-weight surface tension apparatus. 1—stopper, 2—drop tip, 3—electric eye drop counter, 4—drop cup, 5—weight to sink jar, 6—closed atmosphere glass jar, 7—temperature control bath, 8—syringe pump for polymer solution.

according to the method described by Blais.[4] They were dried in a vacuum oven before being used. The solutions were prepared by weighing both polymer and solvent.

The drop-weight method of surface tension measurement in a closed environment was selected for this work because it minimizes atmospheric effects such as solvent loss by evaporation from the solution and moisture uptake and relatively small volumes of solution were required for the measurement. The apparatus constructed to be used in the surface tension measurements is shown in Figure 1. Initially a volume of test solution was placed into the bottom of the vessel and the system allowed to equilibrate for at least one hour. An electric eye inserted between the tip and the receiving weighing bottle was used to count the drops. The drops were delivered at a very slow rate with a Sage syringe pump through Teflon lines.

Very long drop formation times were required to ensure equilibration on the surface of the drops. Drop formation times of over 100 seconds were attainable when required since an "aging" effect was encountered presumably due to the low diffusion rates of polymer, particularly in the high boiling point solvents. The solutions tested were normally binary solvent-polymer solutions, solvent-solvent solutions, or solvent-salt systems. The solute was always at least 0.5% by weight so that the solutions were sufficiently concentrated to require reasonable surface equilibration times.

A variety of capillary tip sizes which delivered the drops were used. This was to accommodate the different ranges of surface tension and density of the solutions tested. A capillary tip of 2.500 mm was used for all the solutions involving NMP, DMA and DMSO. For acetone solutions, a 2.725-mm tip was found to give better values consistent with literature.

The formula used to calculate the surface tension was:

$$W = 2\pi r_B \gamma F\left(r_B / V^{1/3}\right)$$

where,

  $W$ = drop weight

  $r_B$ = capillary tip diameter

  $\gamma$ = surface tension

and $F(r_B/V^{1/3})$ is a correction factor dependent on the ratio of capillary tip radius to the cube root of the drop volume.

Values of $F(r_B/V^{1/3})$ are tabulated in Padday's study.[5]

The surface tension measurements were performed at 20°C due to the availability of literature data on surface tension and ease of temperature control. The information thereby obtained with respect to variance with concentration or relative surface activities will still be valid although the numerical values for the surface tensions will of course be shifted by the temperature changes.

## RESULTS AND DISCUSSION

Surface tension data were collected for a number of systems related to reverse osmosis membrane casting. There are three distinct types of systems which are: (1) Solvent-additive systems, (2) solvent-polymer systems and, (3) casting solutions. The term "additive" is used for substances like $H_2O$, salt, and other minor components which are present in casting solutions which may or may not be solvents for the polymer.

The solvents examined include acetone, DMA, NMP, and DMSO. Figures 2 to 4 show surface tension dependence upon the composition of the solvent
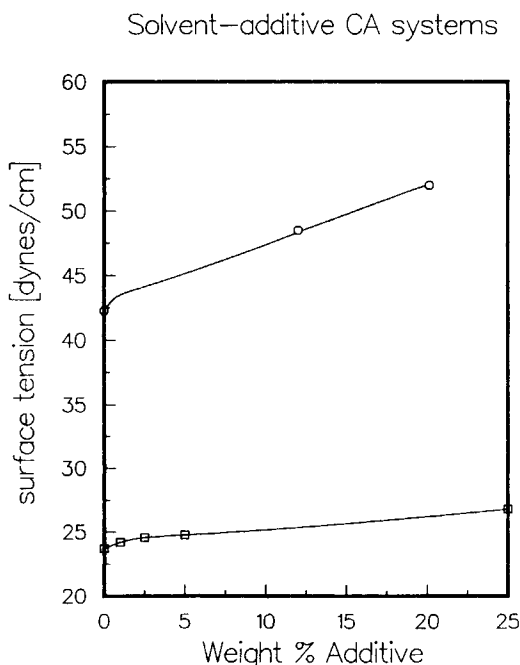


Fig. 2. Surface tension vs. composition data for binary liquid systems related to CA membranes. (□) $H_2O$ in acetone; (○) $H_2O$ in DMSO.
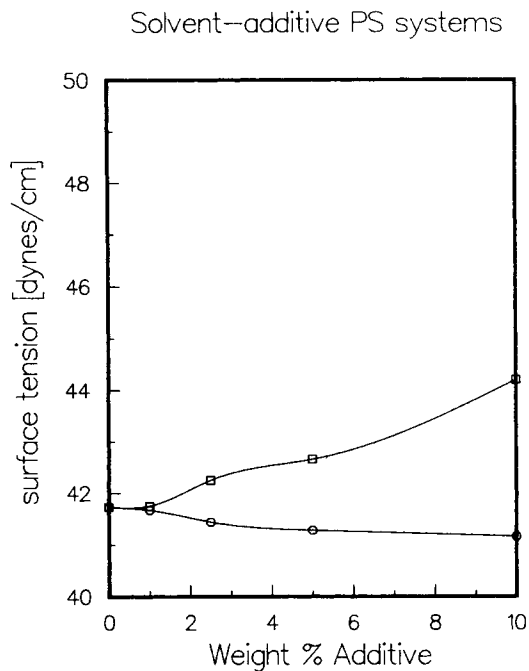
## Solvent—additive PS systems



Fig. 3. Surface tension vs. composition data for binary liquid systems related to PS membranes. (□) $H_2O$ in NMP; (○) PVP in NMP.
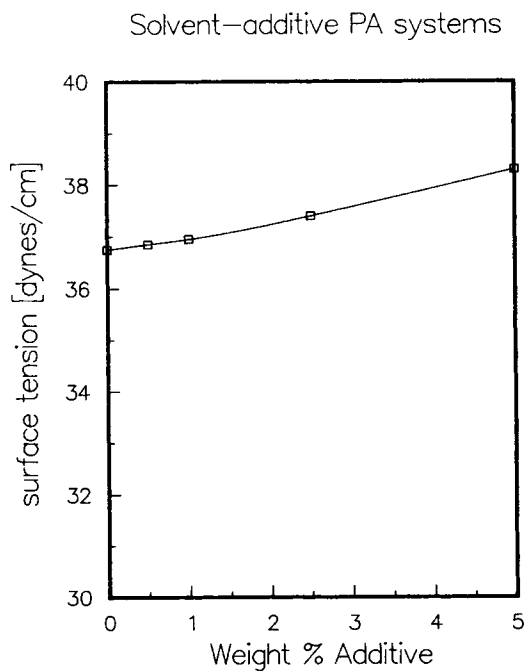
## Solvent—additive PA systems



Fig. 4. Surface tension vs. composition data for binary liquid systems related to PA membranes. (□) $H_2O$ in DMA.

Solvent—salt surface tensions
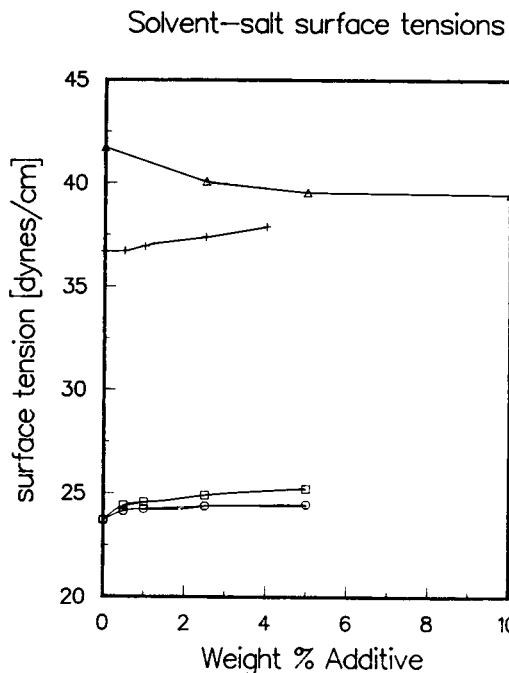


Fig. 5. Surface tension vs. composition data for solvent-salt systems. (□) $Mg[ClO_4]_2[aq.]$ in acetone; (○) $Mg[ClO_4]_2$ in acetone; (△) TEP in NMP; (+) $LiNO_3$ in DMA.

additive systems.[6,7] An increase in surface tension by a substance is an indication that the substance has a negative surface excess at the interface, attributable to the structurization of the solvent. This is the case for $H_2O$ in DMSO, acetone NMP, and DMA. A decrease in surface tension by a substance is an indication of "surfactancy," or a positive surface excess at the interface of the additive substance. PVP in NMP produces this effect.

Surface tensions of salts dissolved in casting solution solvents are plotted in Figure 5. $Mg[ClO_4]_2$ in acetone and $LiNO_3$ in DMA show a negative surface excess, whereas TEP in NMP show a positive surface excess.

The polymers investigated in the work are those which have proved useful in membrane applications or are expected to perform successfully based on the previously outlined criteria for membrane suitability. Polymers such as CA, PA, and PS, were made into solutions of varying concentrations with the aforementioned solvents. CA-DMSO data is from Tanny.[1] Plots of surface tension versus concentration for these solutions are shown in Figure 6. As explained, "surfactancy" occurs for the polymer solutions studied (except for CA in DMSO), which is desirable for membrane-forming polymers dissolved in the previously mentioned solvents.

Finally, surface tension data were collected for different concentrations of two casting solutions. There included a CA-acetone-$Mg(ClO_4)_2$(aq.) system and a CA-acetone-formamide system (Fig. 7).

What is of note about the above data is the surface tensions of the binary/ternary mixture with respect to the surface tensions of the pure
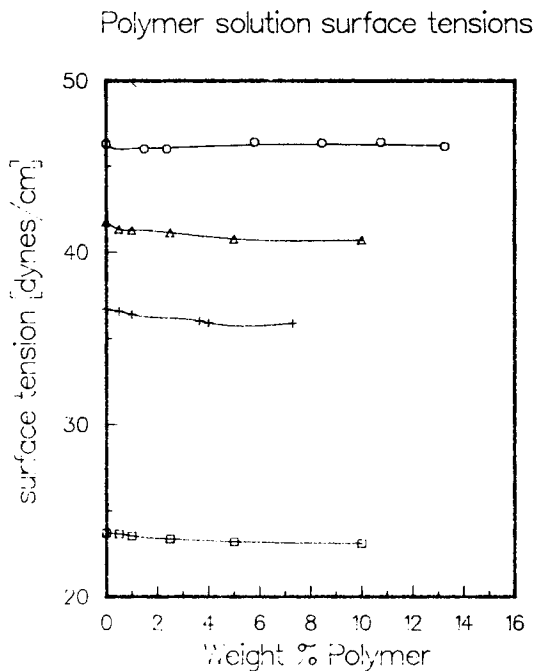
## Polymer solution surface tensions



Fig. 6. Surface tension vs. composition data for solvent-polymer systems. (□) CA in acetone; (○) CA in DMSO; (△) PS in NMP; (+) PA in DMA.
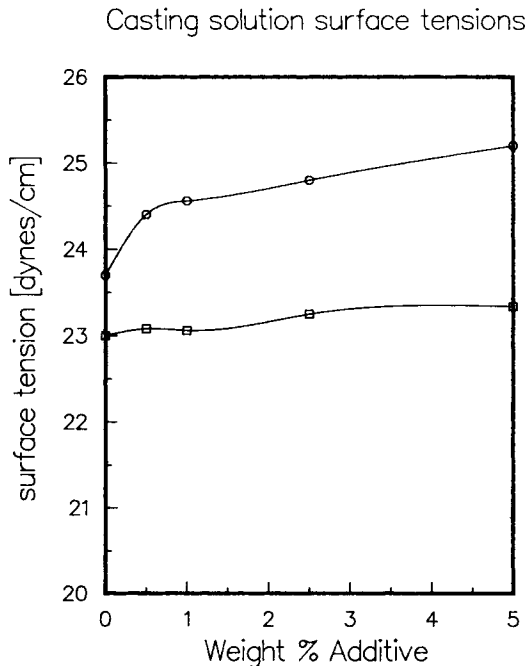
## Casting solution surface tensions



Fig. 7. Surface tension vs. composition data for CA reverse osmosis membrane-casting systems. Casting solution of 5% CA in acetone; (□) HCONH$_2$ in casting solution (25°C); (○) $10^{-2}M$ Mg[ClO$_4$]$_2$[aq.] in casting solution.

constituents of the mixture. This gives information about the relative surface activity of the components.

Since surface tension is essentially a thermodynamic property (i.e., another name for it is surface free energy), surface tension data of binary mixtures can be examined in a way analogous to multicomponent liquid-vapor equilibrium data. The vapor pressure of composite mixtures can be expressed by Raoult's law which states $P_T = \Sigma P_i^* X_i$, where $X_i$ is the mole fraction of the $i$-th component. Similarly, the surface tension of a mixture could be expressed as $\gamma_T = \Sigma \gamma_i X_i$.[8] This is true only for very dilute systems where the concentrations at the surface are too low to form a continuous surface film. Most of the plotted data show either negative or positive deviations from this representation, indicating too high a concentration for the relation to hold. This deviation, called surface excess $\Gamma_2$, can be predicted by the Gibbs adsorption isotherm, $\Gamma_2 = -c_2/RT \, d\gamma/dc_2$.

$C_2$ is additive concentration, $R$ is the universal gas constant, and $T$ is the absolute temperature. It is important to point out that the surface activity that develops in dilute systems, say below 2% concentration, determines the relative surface composition. In these experiments, concentrations up to 12% were used to establish this minimum concentration. The $Mg[ClO_4]_2$ in casting solution, $Mg[ClO_4]_2$ in acetone, $H_2O$ in acetone, and $H_2O$ in DMSO systems illustrate this phenomena in that at very low concentrations there is a sharp initial surface tension increase, then a smaller rate of increase at higher concentrations. The sharp initial surface tension increase implies a large negative surface excess for the additive.

In the simplest situation, successful membrane casting would be achieved with a solvent-polymer system where the surface tension of the polymer solution is less than that of the pure solvent.

The importance of polymer "surfactancy" in the casting of asymmetric membranes can be shown with reference to the acetone-CA and DMSO-CA (Fig. 6) systems. Increasing CA concentration decreases the surface tension of the acetone system but has a lesser effect in DMSO. Reverse osmosis membrane casting work for CA membranes cast in acetone versus those cast in DMSO shows that, as predicted by the surface tension data,[1] a dense polymer film was formed on the membrane surface at the gelation bath in the acetone case, whereas in DMSO, the membranes are "reverse skinned" and thus are more suitable for larger open pore filtration applications.[9]

The importance of dense polymer skin formation on one side of a membrane was explained in an early paper.[2] As an extension to that work, it is now evident that the surface tension of a polymer solution compared to the surface tension of the pure solvent is as informative as would be data from preliminary reverse osmosis separation runs.

Sometimes, the solubility of the polymer in the solvent is itself a consideration. To achieve a high enough polymer concentration for successful membrane casting, it is often required to increase the solubility of the polymer in the solvent by adding a quantity of another solvent or inorganic salt. An example is that PA is sparingly soluble in pure DMA but readily dissolves in DMA-containing salts.

Aside from enhancing the solubilities of polymers in some cases, inorganic salts may be added to casting systems to increase the surface activity of
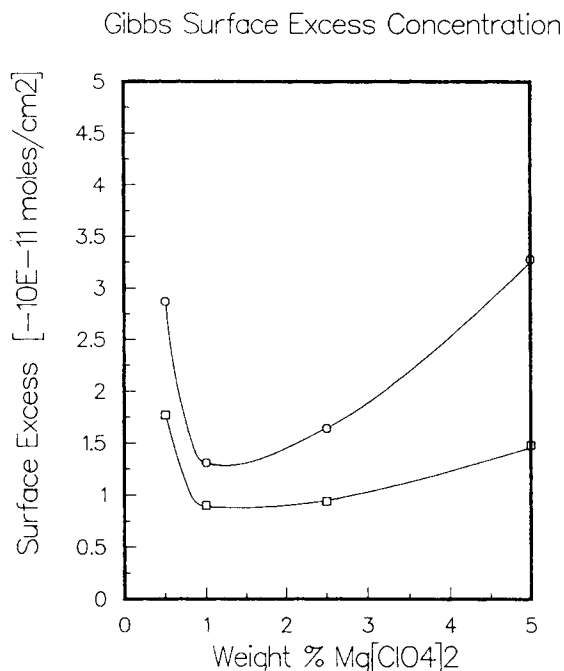
Fig. 8. Surface excess concentration of $Mg[ClO_4]_2$ in pure acetone and an acetone-CA casting system to show how the salt is used to effectuate a superior dense polymer skin for CA membranes. (□) solvent-polymer system; (○) salt-solvent-polymer system.

polymers. Figure 8 is a plot of $\Gamma_2$, the surface excess concentration of $Mg[ClO_4]_2$ in acetone and an acetone-based casting system. The negative surface excess of this salt is greater in magnitude with CA present, in effect promoting CA on the surface and the corresponding formation of a dense skin in a membrane-casting system.

The main application for using surface tension measurements on polymer solutions would be to predict the viability of new additives and polymers or surface tension considerations in conjunction with other considerations such as solubility parameters in different solvent systems for membrane-casting possibilities. Surface tension measurements will confirm their successful performance by showing that the dense polymer layer is formed on the gelation bath side of the membrane, or conversely, a poorer performance resulting from a "reverse skinned" membrane or unskinned at the air interface.[1]

A highly useful and foreseeable application of surface tension data would be to determine the surface activity of the different components in a multicomponent casting system. Work has been done in this area with polydimethylsiloxane systems.[10] It has been established that certain groups or side chains on polymers are desirable on reverse osmosis membrane surfaces for certain applications, and that their presence there could be demonstrated by surface tension measurements and further confirmed by Fourier transform infrared (FTIR) or other analysis.

Eventually, a broader database for surface compositions and surface activities of system components will lead to an understanding of polymer orienta-

tion at membrane surfaces and thereby render design for different applications a more straightforward task. In this light, surface tension data on polymer solutions can be expected to clarify the component interactions in complex systems.

Of further interest for future study are diffusional phenomena prior to the actual equilibration of the surface. Often, the mobility of polymers in organic solvents is low and the surface composition equilibrates slowly. In view of diffusion, time and temperature effects are important not only for the surface tension but for practical membrane-casting considerations as well. Such dynamics of the interfacial layer as expressed by surface tension will be dealt with in later publications.

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