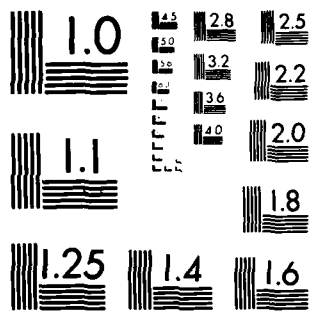


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FRANK J. SEILER RESEARCH LABORATORY

**THE WETTING BEHAVIOR OF
IMIDAZOLIUM-CONTAINING,
ROOM-TEMPERATURE MOLTEN SALT**

J. G. Eberhart

August 1984

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ROOM-TEMPERATURE MOLTEN SALT

J. G. EBERHART

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THE WETTING BEHAVIOR OF IMIDAZOLIUM-CONTAINING,
ROOM-TEMPERATURE MOLTEN SALTS

by

J. G. Eberhart

SUMMARY

A room-temperature, molten-salt system composed of 1-methyl-3-ethylimidazolium chloride plus aluminum chloride has been developed and extensively studied at FJSRL over the last few years. The most promising application of this liquid mixture is as a battery electrolyte, and for this reason a study was undertaken of the wettability of various candidate battery component materials by the molten salt. Advancing and receding contact angles were determined for the binary melt as a function of such variables as mixture composition, chlorination of the imidazolium ion, replacement of AlCl_3 by LiCl , solid porosity, and solid surface cleaning procedure. Measurements were also made of the surface tension of the melt at one composition in the basic range. Surface tension data was helpful in understanding the composition dependence of melt wetting behavior.

PREFACE

The author would like to thank the Air Force Systems Command, the Air Force Office of Scientific Research, and the Southeastern Center for Electrical Engineering Education for providing the opportunity to carry out this research at the Frank J. Sellar Research Laboratory at the U.S. Air Force Academy. In particular, he would like to acknowledge the support of and helpful technical discussions with Lt. Col. Chester J. Dymek, Jr., Lt. Col. Armand A. Fannin, Jr., Dr. John S. Wilkes, and Prof. Francis M. Donahue. The author also extends his thanks to Jeff Boon for the preparation of molten salt samples and to Fred Kibler for helpful suggestions on apparatus design.

I. INTRODUCTION

The wetting behavior of a battery electrolyte can have a dramatic effect on the internal resistance of the battery as well as its cycle life.⁽¹⁾ Good wetting of battery separators and particle retainers by electrolyte is essential to the easy passage of ions through the separator pores during charge and discharge. Good wetting of solid electrodes by electrolyte is also important, whether the electrodes be porous or nonporous. Liquid electrodes must wet the porous structure in which they are loaded and also the current collector (which may be the same material). In addition, it is essential that a liquid electrode preferentially wet these same structures over the electrolyte, so that the electrolyte does not displace the liquid electrode from the current collector. Porous, gas-diffusion electrodes require, on the other hand, a lesser degree of electrolyte wetting, so that the line of contact of the three phases (reactive gas/liquid electrolyte/porous electrode or current collector) can be maintained within the porous current collector through a balance of capillary and hydrostatic pressures.

For several years now a room-temperature, molten-salt system composed of 1-methyl-3-ethylimidazolium chloride ($C_6N_2H_{11}Cl$) plus aluminum chloride has been under study at the Frank J. Seiler Research Laboratory.⁽²⁻⁵⁾ The most promising application of this novel liquid mixture is as a battery electrolyte. Analysis of available physical and electrochemical data suggests that cells with a chlorine positive electrode reactant and a magnesium, aluminum, or zinc negative electrode material are likely candidates.⁽⁶⁾

The ability of a liquid electrolyte to penetrate a porous solid battery material is determined by several physical properties: (1) the contact angle of the liquid on the solid surface, (2) the surface tension of the liquid, and (3) the geometry of the solid's pore structure. Based on these considerations and on consultation with FJSRL personnel, the objectives of this study were formulated and are outlined below.

II. OBJECTIVES

Based on the wetting considerations outlined above, a study was undertaken of the contact angles of various room-temperature molten salts on candidate battery separator and current collector materials. The factors examined in the study were the effects on wettability of: (1) the melt composition, (2) chemical constitution of the solid, (3) chlorination of the organic component of the melt, (4) replacement of the AlCl_3 component by other inorganic compounds, and (5) cleaning procedure for the solid. To aid in the interpretation of the effect of melt composition, some preliminary measurements were also made of the surface tension of one of the melts.

III. THEORY

The wettability of a solid surface is defined in terms of the contact angle, θ , made by a liquid drop resting on the solid surface, as shown in Fig. 1. The angle θ can take on values ranging from 0 to 180 deg. The smaller the angle, the better the liquid is said to wet the solid. The contact angle made by a liquid on a solid can have either one value or a range of possible values, depending on the nature of the solid surface.

If the solid surface is idealized as smooth, chemically homogeneous, isotropic, and nondeformable, and there is no mutual solubility or chemical reaction between the two phases, then there is only one stable, equilibrium contact angle which is given by Young's equation⁽⁷⁾

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (1)$$

where γ_{LV} is the liquid surface tension, γ_{SV} is the solid surface tension, and γ_{SL} is the interfacial tension between the solid and liquid phases. If $0 < \theta < 90$ deg, then the liquid is said to wet the solid and the liquid will spontaneously penetrate pores of the same solid. If $90 \text{ deg} < \theta < 180$ deg, then the liquid does not wet the solid and the liquid will not spontaneously penetrate pores of the same solid. If a hydrostatic pressure is applied to a nonwetting liquid, the liquid can be forced into a capillary system; however, the liquid will spontaneously exit the system when the pressure is removed.

If the solid surface is a real, rather than an ideal, surface, then it will be rough, chemically heterogeneous, and anisotropic and the contacting liquids will have a range of allowed contact angles rather than a single value.⁽⁸⁾ The maximum angle is called the advancing contact angle, θ_A , while the minimum angle is called the receding contact angle, θ_R . The difference $\theta_A - \theta_R$ is the contact-angle hysteresis. The fact that these systems have a range of contact angles leads to a more complex categorization of wetting behavior.⁽⁹⁾ If $\theta_R < \theta_A < 90$ deg, then the solid is easy to wet by the liquid and the liquid will spontaneously penetrate pores of the same solid. If 90 deg $< \theta_R < \theta_A$, then the solid is difficult to wet by the liquid and the liquid will not spontaneously penetrate pores of the same solid. However, if the liquid is forced into these pores by the application of a hydrostatic pressure, it will remain in the pores after the pressure is removed. Finally, if 90 deg $< \theta_R < \theta_A$, then the solid is impossible to wet by the liquid and the liquid will not spontaneously penetrate pores of the same solid. If the liquid is forced into these pores, it will spontaneously leave the pores when the force is removed.

For real solid surfaces there are also situations involving mutual solubility or chemical reaction between the two phases. Wetting theory has been extended to allow for these possibilities.⁽¹⁰⁾

The advancing and receding contact angles are determined from observation of a tilting sessile drop,⁽⁸⁾ as pictured in Fig. 2. If the angle of the tilt of a drop, α , is increased, then the upper and lower contact angles, θ_U and θ_L , will approach limiting values of θ_R and θ_A , respectively. Increasing the tilt until constant or extreme values of θ_U and θ_L are obtained thus yields θ_R and θ_A .

In addition to providing θ_R and θ_A , Macdougall and Ockrent⁽¹¹⁾ have shown how the measurement of θ_U and θ_L as a function of α can also be used to determine the liquid surface tension γ_{LV} . If a capillary and gravitational force balance is performed on a lamina taken through the center of gravity of the drop,

at right angles to the plane of the surface and to the axis of inclination, then the resulting equation is

$$\gamma_{LV} \cos \theta_U = \gamma_{LV} \cos \theta_L + \rho g A \sin \alpha \quad (2)$$

where ρ is the density difference between the liquid and vapor phases, g is the gravitational acceleration, and A is the cross-sectional area of the drop as viewed from the side (as in Fig. 2). In the absence of evaporation A is a constant independent of α . (11) Eq. (2) is easily rearranged to give

$$\cos \theta_U - \cos \theta_L = (\rho g A / \gamma_{LV}) \sin \alpha \quad (3)$$

Thus, if θ_U and θ_L vary with α , a plot of $\cos \theta_U - \cos \theta_L$ versus $\sin \alpha$ will be linear with zero intercept and a slope of $\rho g A / \gamma_{LV}$. Often a drop is delivered to a horizontal surface in such a way that its contact angle is θ_A . In this case θ_U will decrease with α but $\theta_L = \theta_A$ will remain constant. For this situation Eq. (3) is put in the form

$$\cos \theta_U = \cos \theta_A + (\rho g A / \gamma_{LV}) \sin \alpha \quad (4)$$

and a plot of $\cos \theta_U$ versus $\sin \alpha$ will again have a slope of $\rho g A / \gamma_{LV}$, but an intercept of $\cos \theta_A$. Of course, with either of these versions of the tilting drop analysis, it is necessary to not only measure θ_U and θ_L as functions of α , but to also observe the x and y coordinates of the drop profile so that A can also be determined. With a knowledge of ρ , g , and A , the surface tension is easily calculated from the slope of either of the plots described above.

IV. EXPERIMENTAL METHODS

The salts 1-methyl-3-ethylimidazolium chloride ($C_6N_2H_{11}Cl$) and aluminum chloride are reactive with air and moisture, so the preparation of their mixtures at various compositions and the determination of contact angles on various solid surfaces was carried out entirely within a helium glovebox having moisture and oxygen concentrations of less than 10 ppm. (2) These salts were prepared at four different concentrations with $AlCl_3$ mole fractions, N , of

0.333, 0.500, 0.600, and 0.667. This choice covers the range of basic ($N < 0.5$), neutral ($N = 0.5$) and acidic ($N > 0.5$) behavior and was selected to show the effect of melt concentration on wetting behavior.

Mixtures were also prepared of the chlorinated imidazolium salt ($C_6N_2H_9Cl_3$) with aluminum chloride at $AlCl_3$ mole fractions of 0.375, 0.600, and 0.650, to assess the effect of chlorination on wetting behavior.

A mixture of the imidazolium salt with lithium chloride was also prepared with a $LiCl$ mole fraction of 0.376 to examine the effect of the $AlCl_3$ on wetting behavior.

A simple tilting stage was assembled out of lattice rod and clamps. It can hold substrates of interest (whether rigid or film) in any orientation from horizontal to vertical. The contact angles, tilt angles, and drop dimensions were observed through the glovebox window with a Gaertner telemicroscope equipped with a goniometer and two X-Y positioning micrometers.

The substrates examined were soda-lime glass microscope slides, Teflon (Berghof/America, Inc.), Celgard 2500 and 3501 polypropylene film (Celanese Corp.) with 45% porosity and 0.04- μm pore size, and reticulated vitreous carbon or RVC (Energy Research and Generation, Inc.) with a 97% porosity and 70-90 pores per inch.

The substrates were cleaned in various ways. The soda-lime glass was washed either with Alconox or with Chromerge, and then rinsed with water and with ethanol. The Celgard films and the RVC were washed in ethanol. Although the two Celgard films have the same mechanical properties and pore structure, the Celgard 3501 is hydrophilic because of treatment with a proprietary surfactant. As a result, the Celgard 3501 is more wettable by aqueous systems than the hydrophobic Celgard 2500. This difference could be observed during cleaning of the two films with ethanol. The films are white and opaque, but when the 3501 was contacted with ethanol it became momentarily transparent. A Celanese technical representative attributed this behavior to the pore filling of the 3501 film and its resultant change in optical properties.

V. EXPERIMENTAL RESULTS

The advancing and receding contact angles for a number of different room-temperature, imidazolium-containing molten salts were determined on the substrates described above using the tilting drop technique at temperatures in the range of 27-28°C. The first three columns in Table I show some typical data for the contact angles of a melt of 1-methyl-3-ethylimidazolium chloride plus aluminum chloride at the upper and lower ends of the melt drop. This melt has an AlCl_3 mole fraction of 0.333. The contact angles were measured as a function of tilt angle α at a temperature of 27.3°C. Since the values of θ_L are essentially constant with α , an average value of $\theta_A = 77$ deg was selected for the advancing angle. Since θ_U decreases with α , a minimum value of $\theta_R = 48$ deg was selected for the receding angle, corresponding to the largest possible value of α . When α was further increased, the drop rolled off the substrate. (The fourth and fifth columns of Table I will be discussed later.) Advancing and receding contact angles for other melts and other substrates were similarly determined and are summarized in Tables II-IV.

The advancing and receding contact angles for the 1-methyl-3-ethylimidazolium chloride plus aluminum chloride melts on glass, Teflon, polypropylene, and RVC surfaces are shown in Table II. All of the substrates except the RVC are easy to wet by the melt with spreading observed for several acidic melts on glass. RVC is difficult to wet by basic and neutral melts.

The contact angles for chlorinated melts of 1-methyl-3-ethylimidazolium chloride plus aluminum chloride on glass surfaces are shown in Table III. Glass is easy to wet by the chlorinated melt.

Table IV shows the results of replacing AlCl_3 by LiCl in the 1-methyl-3-ethylimidazolium chloride melts. Glass and Celgard 2500 substrates were found to be difficult to wet by a basic melt of this system.

A preliminary determination of the surface tension of a basic melt ($N = 0.333$) of 1-methyl-3-ethylimidazolium chloride plus aluminum chloride was also carried out on a Teflon substrate at 27.3°C. The

contact angles at the upper and lower ends of the drop were previously shown in Table I as a function of the substrate tilt angle α . Because θ_L is essentially constant, the data was fit to Eq. (4) and $\sin \alpha$ and $\cos \theta_U$ were computed in the fourth and fifth columns of Table I. The x and y coordinates of the drop profile and the solid surface were also determined for the $\alpha = 0.5$ deg configuration. The points were plotted on graph paper, a smooth curve was drawn through the points, and the cross-sectional area of the drop was determined by cutting out the drop outline and weighing the outline as well as a reference rectangle on an analytical balance. The area was determined to be $A = 0.06161 \text{ cm}^2$. The density of the drop was calculated from the published density-temperature-mole fraction relationship for this system⁽⁵⁾ which yielded $\rho = 1.2313 \pm 0.0004 \text{ g cm}^{-3}$. The local acceleration of gravity was taken to be $g = 979.4 \text{ cm s}^{-2}$. The data in Table I was used to construct a plot of $\cos \theta_U$ versus $\sin \alpha$. The results are shown in Fig. 3. A linear regression line was fit through the data which yields a slope of $\rho g A / \gamma_{LV} = 1.159 \pm 0.076$ and an intercept of $\cos \theta_A = 0.239 \pm 0.016$. The overall standard deviation of the straight line is ± 0.026 . These results give a surface tension for the melt of $\gamma_{LV} = 63.0 \pm 4.1 \text{ dyn cm}^{-1}$ and an advancing contact angle of $\theta_A = 76 \pm 1 \text{ deg}$.

There is very little information in the technical literature on the wetting behavior or the surface tension of AlCl_3 -containing binary molten salt systems. In a study of the surface tension of sodium chloride plus aluminum chloride melts, Dewing⁽¹²⁾ commented that these melts wet glass. This result is consistent with the easy-to-wet behavior described here for 1-methyl-3-ethylimidazolium chloride plus aluminum chloride melts on glass.

The wettability of battery component materials by other molten salts, such as lithium chloride plus potassium chloride, has been shown to be much improved by the application of LiAlCl_4 to the surface.^(1,13) The effectiveness of this AlCl_3 -containing wetting promoter is also consistent with the good wetting generally observed in the present study for room-temperature molten salts containing AlCl_3 .

The surface tension of pure molten AlCl_3 has also been determined as a function of temperature.⁽¹⁴⁾ When these results are extrapolated to 27.3°C (a supercooled liquid state) they yield a surface tension of $\gamma_{LV} = 23.6 \text{ dyn cm}^{-1}$. This is much lower than the value determined above for the melt with $N = 0.333$, and suggests that the surface tension of the 1-methyl-3-ethylimidazolium chloride plus aluminum chloride decreases strongly with increasing AlCl_3 mole fraction.

VI. CONCLUSIONS

An examination of the data presented in the last section suggests the following: (1) The 1-methyl-3-ethylimidazolium chloride plus aluminum chloride melts show easy-to-wet behavior on all substrates tested except RVC. The RVC is difficult to wet by basic or neutral melts and easy to wet by acidic melts. (2) With only one minor exception (Celgard 3501), wetting behavior improves as the mole fraction of AlCl_3 increases. (3) On glass surfaces the chlorination of the 1-methyl-3-ethylimidazolium chloride has relatively little effect on the melt's wetting behavior. (4) When aluminum chloride is replaced by lithium chloride the easy-to-wet behavior on most surfaces changes to difficult-to-wet behavior. (5) The treatment of polypropylene film with a surfactant to change the surface from a hydrophobic to a hydrophilic nature has little effect on the wettability of the surface by the molten salts studied here. (6) The way in which a surface is cleaned can have a dramatic effect on its wettability.

These conclusions, coupled with the limited literature data^(1,12,13) described earlier, suggest that AlCl_3 plays a key role in the wetting behavior of these molten salt mixtures. The surface tension data outlined in the previous section indicates that as the mole fraction of AlCl_3 increases in the melt, the surface tension decreases considerably. The well-known wetting correlations of Zisman^(15,8) show that generally a decrease in liquid surface tension causes a decrease in advancing contact angle. Thus, the improvement in solid-surface wettability as the mole fraction of

AlCl_3 increases in the melt, is probably directly attributable to the fact that the surface tension of AlCl_3 is much lower than that of most molten salts. This is probably the result of the molecular rather than ionic structure of liquid AlCl_3 .

VII. RECOMMENDATIONS

Implementation. The conclusions drawn in the previous section lead to a number of suggestions for the application of these results to molten-salt battery systems. (1) It is not expected that any serious problems will be encountered with the wetting of battery separators and current collectors, especially in the acidic range of concentrations. (2) It is possible that electrolyte wetting may be better than desired in the case of liquid or gaseous electrode reactants. If such problems should occur, it is likely they could be remedied by a decrease in the AlCl_3 mole fraction without serious impairment of separator and current-collector wettability. (3) If chlorinated melts are used in original cell designs or produced as a result of a chlorine gas positive electrode, their wetting behavior is likely to be about the same as the nonchlorinated melts. (4) If electrolytes are considered without AlCl_3 as the inorganic component, then the generally favorable wetting picture presented here could change dramatically for the worse.

Follow-on research. The contact-angle measurements described here provide an indication of whether a melt will or will not penetrate the pores of a battery component. However, if one wishes to know the extent to which penetration will take place, then it is necessary to determine the adhesion tension of the melt, β , which is defined as

$$\beta = \gamma_{LV} \cos \theta \quad (5)$$

The best known example of the use of the adhesion tension is probably in the calculation of the height of rise of liquid in a vertical capillary tube

$$h = 2\gamma_{LV} \cos \theta_A / \rho g r \quad (6)$$

where r is the radius of the capillary.

If it is further desired to predict the rate of filling of a porous structure, then it is also necessary to know the viscosity, η , of the liquid. The Washburn equation provides the simplest example of wetting kinetics. For a horizontal capillary (or a vertical tube where gravitation can be neglected) the time dependence of the liquid column length is given by

$$h^2 = 2rt\gamma_{LV} \cos \theta_A / 2\eta \quad (7)$$

Previous studies at FJSRL⁽⁵⁾ have determined the density ρ and viscosity η of these melts. But as yet no extensive measurements have been made of the melt surface tension γ_{LV} .

The surface tension of a melt is also a valuable physical property for providing insight into the molecular or ionic structure of a melt⁽¹⁶⁻¹⁸⁾ because of its dependence on molecular or ionic size, as well as complex ion formation.

Thus, surface tension measurements on imidazolium-based melts would be of great practical value for predicting the extent and rate of pore penetration, and of considerable theoretical interest in further elucidating the liquid structure.

The tilting drop technique employed in this study for a preliminary surface tension estimate is not considered an ideal technique. It suffers from limited precision, lengthy measurement and computation time, impossibility of use with a liquid that spreads, and difficulty with temperature control. One of the more classical techniques of measurement such as the du Noüy ring or the maximum bubble pressure method is suggested. Techniques such as capillary rise or Wilhelmy slide are not recommended because they actually measure the adhesion tension rather than the surface tension.

Thus, measurement of the surface tension of the 1-methyl-3-ethylimidazolium chloride plus aluminum chloride melt as a function of temperature and composition is suggested as a valuable addition to the existing body of knowledge on this interesting system.

The tilting drop technique. A final comment is provided on the use of the tilting-drop technique for surface-tension determination.

The theoretical analysis of Macdougall and Ockrent⁽¹¹⁾ has been employed in this study. Their Eq. (3) suggests that $\cos \theta_U - \cos \theta_L$ is directly proportional to $\sin \alpha$, with a slope of $\rho g A / \gamma_{LV}$. A number of other authors^(8,19-21) suggest the alternative equation

$$\cos \theta_U - \cos \theta_L = (Mg/L\gamma_{LV}) \sin \alpha \quad (8)$$

where M is the mass of the drop, and L is the maximum width of the drop base when viewed from the direction of solid surface inclination. This equation also indicates that $\cos \theta_U - \cos \theta_L$ is proportional to $\sin \alpha$, but predicts a different slope of $Mg/L\gamma_{LV}$. These two slopes cannot be the same unless $\rho A = M/L$ or $\rho = M/AL$. But AL is not the volume of the inclined drop because A is the maximum cross-sectional area and L can be the maximum width in the case of a wetting drop. Thus, AL is quite different than the drop volume. A theoretical analysis by Larkin⁽²²⁾ shows that the slope of Eq. (8) is in error by about 37% for water. His analysis is based on several assumptions including: (1) the contact angle of an inclined drop varies with position around the solid-liquid-vapor contact line, and (2) at a point on this line where the normal, which lies in the inclined surface, is perpendicular to the gravity vector, the contact angle has its horizontal-orientation value. Although the validity of Eq. (3) and the error of Eq. (8) seems relatively certain at this time, future experiments using the tilting-drop method might well benefit from examination of the drop from above (perpendicular to the inclined substrate) and from the direction of inclination of the substrate as a further test of the assumptions of Larkin.

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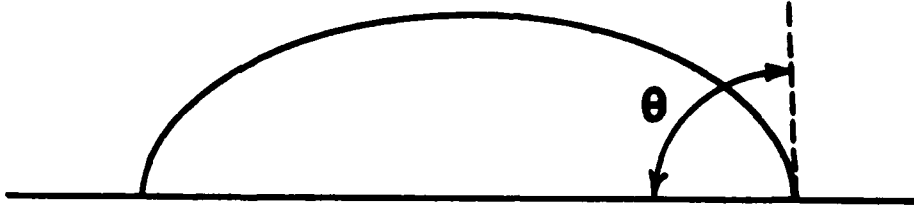


Fig. 1. The contact angle of a liquid on a solid surface.

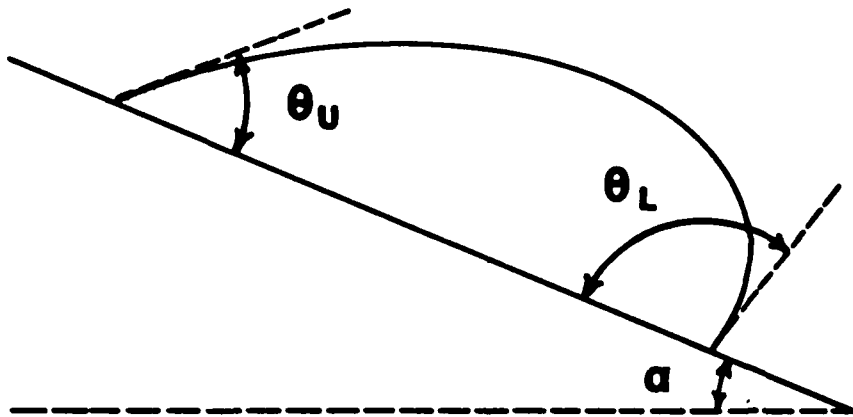


Fig. 2. The upper and lower contact angles of a liquid drop on an inclined solid surface.

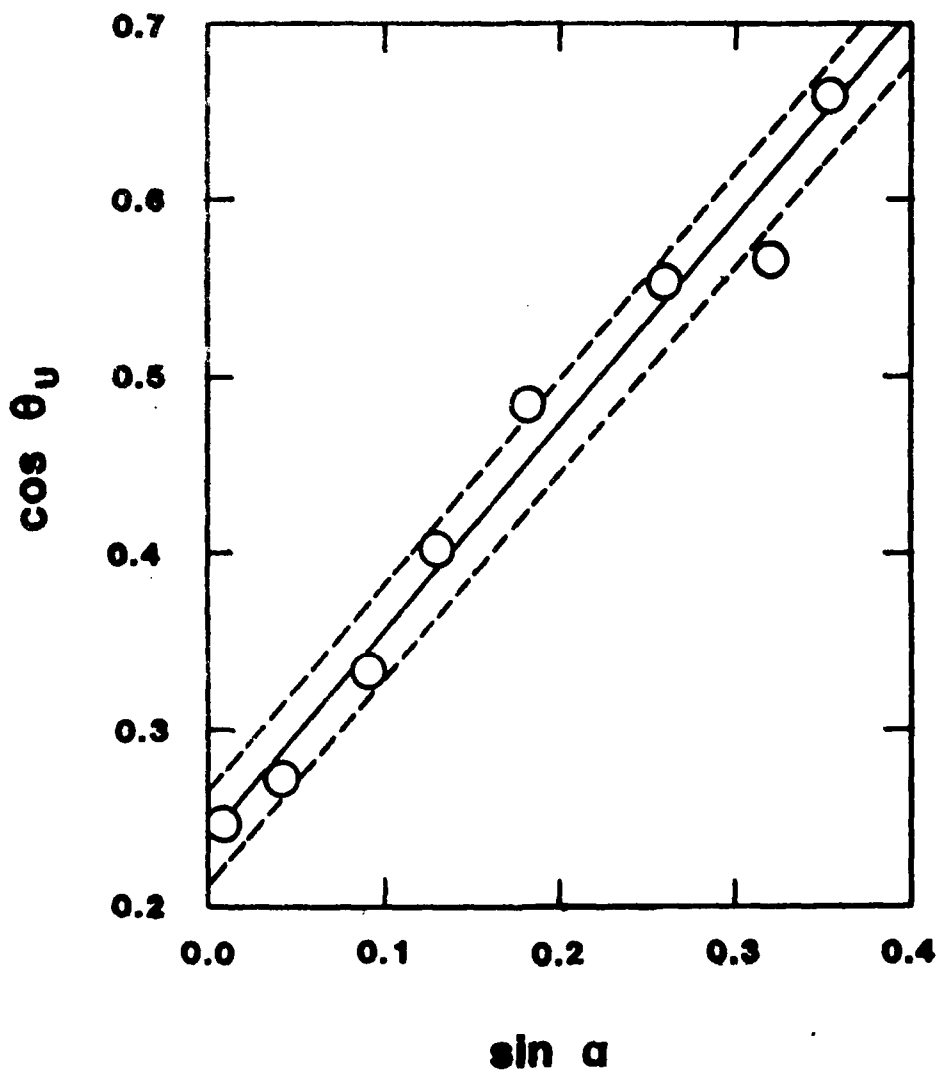


Fig. 3. Contact and tilt angle relationship for a melt with an AlCl_3 mole fraction of 0.333 on a Teflon surface.

Table I

Contact angles at the upper and lower end of a 1-methyl-3-ethylimidazolium chloride plus aluminum chloride melt on Teflon with an AlCl_3 mole fraction of 0.333 at 27.3°C.

α/deg	θ_U/deg	θ_L/deg	$\sin \alpha$	$\cos \theta_U$
0.5	75.7	75.8	0.0087	0.2470
2.4	74.2	78.6	0.0419	0.2723
5.2	70.5	75.7	0.0906	0.3338
7.5	66.3	78.2	0.1305	0.4019
10.5	60.9	76.5	0.1822	0.4863
15.0	56.4	77.5	0.2588	0.5534
18.7	55.4	79.0	0.3206	0.5678
20.7	48.7	75.5	0.3535	0.6600

Table II

Advancing and receding contact angles for 1-methyl-3-ethylimidazolium chloride ($C_6N_2H_{11}Cl$) plus aluminum chloride on various substrates.

Substrate/Cleaning	N	θ_A /deg	θ_R /deg
glass/Alconox	0.333	65	13
	0.500	59	15
	0.600	0	0
	0.667	0	0
glass/Chromerge	0.333	33	8
	0.500	32	7
	0.600	17	6
	0.667	0	0
Teflon/ethanol	0.333	77	48
	0.500	77	48
	0.600	60	23
	0.667	0	0
Celgard 2500/ethanol	0.333	74	32
	0.500	69	--
	0.600	58	19
	0.667	51	8
Celgard 3501/ethanol	0.333	74	25
	0.500	73	39
	0.600	51	0
	0.667	63	0
RVC/ethanol	0.333	108	32
	0.500	100	41
	0.600	penetrated pores	
	0.667	penetrated pores	

Table III

Advancing and receding contact angles for chlorinated 1-methyl-3-ethylimidazolium chloride ($C_6N_2H_9Cl_3$) plus aluminum chloride on glass.

Substrate/cleaning	N	θ_A /deg	θ_R /deg
glass/Chromerge	0.375	50	15
	0.600	16	4
	0.650	0	0

Table IV

Advancing and receding contact angles for 1-methyl-3-ethylimidazolium chloride ($C_6N_2H_{11}Cl$) plus lithium chloride on various substrates.

Substrate/cleaning	N	θ_A /deg	θ_R /deg
glass/Chromerge	0.376	115	9
Celgard 2500/ethanol	0.376	112	52