T_0 = temperature of feed, °K
T = reactor temperature, °K
X_N = number average chain length
θ = residence time, s

LITERATURE CITED

Ausikaitis, J., and A. J. Engel, "Steady State Multiplicity and Stability in an Adiabatic Controlled Cycled Stirred Reactor," *AIChE J.*, **20**, 256 (1974).

Boundy, R. H., and R. F. Boyer, *Styrene, Its Polymers, Copolymers and Derivatives*, p. 157, Reinhold, New York (1952).

Chang, M., and R. A. Schmitz, "Feedback Control of Unstable States in a Laboratory Reactor," *Chem. Eng. Sci.*, **30**, 837 (1975).

Chen, H. T., P. A. Chartier, S. Settachayanon and F. B. Hill, "Influence of Initiation Modes on Stability and Control of a Chain Reacton," paper presented at 71st Annal Meeting of AIChE, Miami Beach, Fla. (Nov., 1978).; also, Polymer Eng. Sci. (1980).

Chen, H. T., and F. B. Hill, "Radiation-Induced Polymerizations in Continuous Stirred-Tank Reactors," *AIChE J.*, **17**, 933 (1971).

Chen, H. T., and J. Steernod, "Effects of Mixing on Polymerizations in Batch Reactors: Comparison of Catalytic and Ionizing Radiation Initiations," *Polymer Eng. Sci.*, **15**, 357 (1975).

Guha, B. K., G. Narsimhan and J. B. Agnew, "Transient Behavior of an Adiabatic Continuous-flow Stirred Tank Reactor," *Ind. Eng. Chem. Fundamentals*, **14**, 146 (1975).

Hashimoto, S., and W. Kawakami, "Experimental Study on Control of Radiation Polymerization by Dose Rate Regulation," *Ind. Eng. Chem. Process Design Develop.*, **15**, 244 (1976*a*).

——————., and T. Akehata, "A Study on Control of Radiation Polymerization by Dose Rate Regulation," *ibid.*, **15**, 549 (1976*b*).

Hatchard, C. G., and C. A. Parker, "Sensitive Chem. Actiometer (II) K Ferrioxalate as a Standard Chem. Actiometer," *Proc. Royal Soc. (London)*, **A235**, 518 (1956).

Hill, F. B., and H. T. Chen, "Radiation Initiation of Exothermic Reactions," paper presented at 164th ACS National Meeting, New York (Aug., 1972).

Hoftyzer, P. J., and Th. N. Zwietering, "Characteristics of a Reactor for the Homogeneous Polymerization of Ethylene," *Chem. Eng. Sci.*, **14**, 241 (1961).

Ibarra, M., and J. M. Smith, "Induction-period Kinetics in Acrylamide Photopolymerization," *AIChE J.*, **20**, 404 (1974).

Jain, R. L., W. W. Graessley and J. S. Dranoff, "Design and Analysis of a Photoreactor for Styrene Polymerization," paper presented at the 3rd Joint Meeting AIChE and Puerto Rican Inst. Chem. Eng., San Juan (1970).

Mendiratta, S. K., R. M. Felder and F. B. Hill, "Benzoin- and Benzoin Methyl Ether-sensitized Photopolymerization of Styrene and Methyl Methacrylate: Quantum Yield and Mixing Effects," *AIChE J.*, **21**, 1115 (1975).

Sandru, D., and J. M. Smith, "Photopolymerization of Acrylamide in an Annular Flow Reactor," *ibid.*, **19**, 558 (1973).

Vejtasa, S. A., and R. A. Schmitz, "Steady State Multiplicity and Stability in an Adiabatic Stirred Reactor," *ibid.*, **16**, 410 (1970).

Warden, R. B., and N. R. Amundson, "Stability and Control of Addition Polymerization Reactions," *Chem. Eng. Sci.*, **17**, 725 (1962).

Yemin, L., and F. B. Hill, "Measurement of Effects of Mixing of Chain Centers in a Nonuniformly Initiated Photopolymerization," *Ind. Eng. Chem. Fundamentals*, **8**, 210 (1969).

Manuscript received October 1, 1979; revision received January 3, and accepted Janury 21, 1980.

Miscibility Limits for Salt Containing Systems

R. W. ROUSSEAU

Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27650

Nonvolatile salts have been shown to influence phase equilibrium behavior (Long and McDevit, 1952; Johnson and Furter, 1957, 1960; Meranda and Furter, 1974), and considerable effort has been expended on developing models that are useful in correlating and predicting salt effects on phase equilibrium. Most of this effort, however, has been focused on vapor-liquid equilibria, with little work done on partially miscible systems. In this paper, a method for estimating miscibility limits of binary solvents will be presented. The procedure is an extension of the model proposed by Boone, Rousseau and Schoenborn (1976) and refined by Rousseau and Boone (1978) for correlating and predicting vapor-liquid equilibria in salt containing systems.

IMMISCIBILITY

A liquid solution will separate into two phases if the resultant free energy is less than that of the original mixture. For a binary system, the specific Gibbs free energy can be written in terms of the excess free energy as

$$g = g^E + g^{\text{ideal}} \qquad (1)$$

where

$$g^{\text{ideal}} = x_1 g_1^{\text{pure}} + x_2 g_2^{\text{pure}} + RT(x_1 \ln x_1 + x_2 \ln x_2) \qquad (2)$$

so that

$$g = g^E + x_1 g_1^{\text{pure}} + x_2 g_2^{\text{pure}} + RT(x_1 \ln x_1 + x_2 \ln x_2) \qquad (3)$$

Recognizing that phase separation requires downward concavity of the function g, Prausnitz (1969) gives as a criterion for solution instability

$$\left(\frac{\partial^2 g}{\partial x_1^2}\right)_{T,\,P} < 0 \qquad (4)$$

Recalling the definition of the excess Gibbs free energy

$$g^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad (5)$$

and activity

$$a_i = x_i \gamma_i \qquad (6)$$

we can show that

$$g = RT(x_1 \ln a_1 + x_2 \ln a_2) + x_1 g_1^{\text{pure}} + x_2 g_2^{\text{pure}} \qquad (7)$$

It then follows that the onset of solution instability occurs at the conditions

$$\left(\frac{\partial \ln a_1}{\partial x_1}\right)_{T,\,P} = 0 \qquad (8)$$

and

$$\left(\frac{\partial^2 \ln a_1}{\partial x_1^2}\right)_{T,\,P} = 0 \qquad (9)$$

0001-1541-80-3765-0675-$00.75. © The American Institute of Chemical Engineers, 1980.

Substitution of solution model expressions into Equations (8) and (9) can result in limits on model parameters that set the immiscibility range for any solution following the model. This approach is difficult for all but the simplest solution models. Brandani (1974) has used the van Laar equation

$$\ln \gamma_1 = \frac{A(1 - x_1)^2}{[(1 - x_1) + Qx_1]^2} \tag{10}$$

where $Q = A/B$, for this purpose. Substituting Equation (10) into Equation (8), we get

$$\frac{1}{x_1} - \frac{2AQ(1 - x_1)}{[(1 - x_1) + Qx_1]^3} \tag{11}$$

Two roots to Equation (11) and, therefore, solution instability exist if

$$Q \geq 1 \tag{12}$$

and, according to Brandani,

$$A > \frac{1}{2[Q]([Q] + 1)} \frac{(Q + [Q])^3}{Q} \equiv I_{PB} \tag{13}$$

The symbol $[Q]$ indicates the integer part of Q. Inequality (13) is an empirical approximation to the actual requirements given later by Heidemann (1975):

$$A > [2(1 - Q + Q^2)^{3/2} - (2 - 3Q - 3Q^2 + 2Q^3)]/2Q \equiv I_{PH} \tag{14}$$

SALT SOLUTION MODEL

Rousseau and Boone (1978) presented a solution model for a single salt dissolved in two solvents. The model called for defining two pseudo components: one was the salted in solvent plus salt at a fixed concentration, while the other was the pure second solvent. Using these definitions, vapor-liquid equilibrium data for methanol-water solutions with five separate salts, ethanol-water solutions with lithium chloride and 1-propanol-water solutions with lithium chloride were correlated by Wilson and UNIQUAC equations (Abrams and Prausnitz, 1975).

It was demonstrated in this and earlier work (Boone, Rousseau and Schoenborn, 1976) that predictions of the influence of a nonvolatile salt on the vapor-liquid equilibrium behavior of a binary solvent mixture could be expressed through the use of infinite dilution activity coefficients

$$\frac{\gamma_{1^*}^{\infty}}{\gamma_{1'}^{\infty}} = \frac{1}{x_2^{\infty}} \frac{P_1^s(2)}{P_1^s(2^*)} \exp(k_s C_e) \tag{15}$$

and

$$\frac{\gamma_{2^*}^{\infty}}{\gamma_{2'}^{\infty}} = \frac{P_2^s(1)}{P_2^s(1) - \Delta P_2^s} \tag{16}$$

All that is required for application of these equations are the single salt parameter k_s and vapor pressure lowering of component 2 as a function of salt concentration. Values of these parameters were determined by Rousseau and Boone (1978) and Boone (1976). The experimental work of Rousseau and Boone (1978) showed that solutions of 1-propanol-water with lithium chloride separated into two phases when the salt to water ratio corresponded to that of about a 4 molal mixture.

It would be useful if the model described previously could be used to predict conditions under which a salt containing system became unstable. This paper shows such an extension is feasible and indicates that the empirical criteria of Brandani (1974) provides a better measure of instability than the criteria of Heidemann (1975). It also shows that use of the UNIQUAC equation to determine infinite dilution activity coefficients provides better results than the Wilson equation.

1-PROPANOL-WATER-LITHIUM CHLORIDE

Conditions for solution instability as defined by Equations (8) to (14) are for systems at constant temperature and pressure, whereas the experimental data of Boone (1976) are at constant pressure but not temperature. However, since the temperature variation over the composition ranges was modest, the influence of temperature on model parameters may be ignored.

Equilibrium data on the 1-propanol-water-lithium chloride system were taken at 1 atm and fit with both the Wilson and UNIQUAC equations. The solutions were mixtures of 1-propanol with 0, 1, 2 and 4 molal lithium chloride solutions. Infinite dilution activity coefficients determined from both Wilson and UNIQUAC equations were used to evaluate Van Laar

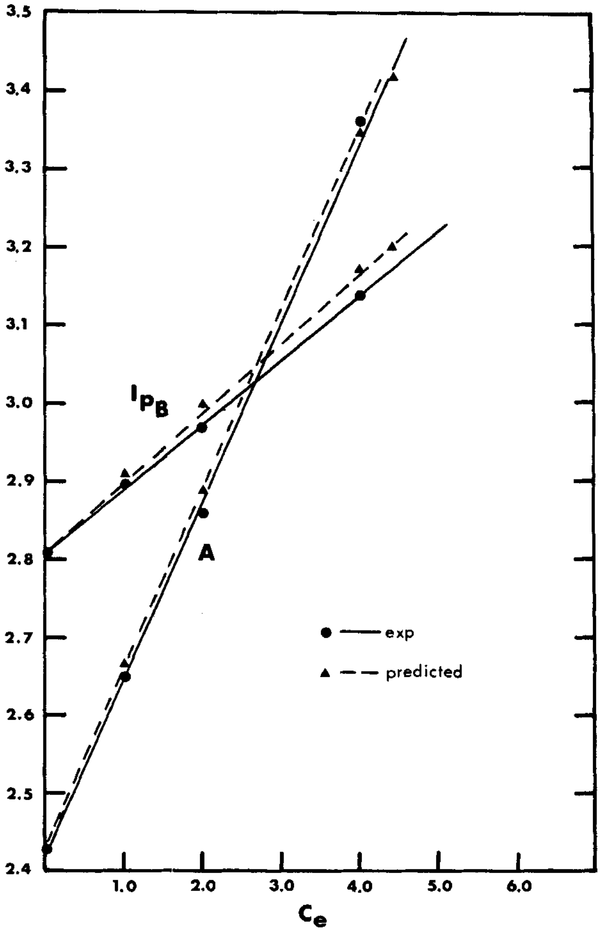

Figure 1. Brandani stability parameters and van Laar constants.

TABLE 1. SUMMARY OF DATA ANALYSIS

Correlating equation	Wilson						UNIQUAC					
C_e	$\gamma_{1^*}^{\infty}$	$\gamma_{2^*}^{\infty}$	A	B	I_{PB}	I_{PH}	$\gamma_{1^*}^{\infty}$	$\gamma_{2^*}^{\infty}$	A	B	I_{PB}	I_{PH}
0.0	21.7	3.31	3.08	1.20	3.10	2.76	11.36	3.00	2.43	1.10	2.81	2.67
1.0	26.2	3.39	3.27	1.22	3.18	2.78	14.17	3.14	2.65	1.14	2.90	2.70
2.0	33.3	3.53	3.51	1.26	3.29	2.80	17.53	3.27	2.86	1.18	2.97	2.72
4.0	52.3	3.96	3.96	1.38	3.35	2.82	28.8	3.59	3.36	1.28	3.14	2.79

TABLE 2. SUMMARY OF PREDICTIONS FROM EQUATIONS (15) AND (16)

	Wilson: $\gamma_{1'}^{\infty} = 21.7$; $\gamma_{2'}^{\infty} = 3.31$						UNIQUAC: $\gamma_{1'}^{\infty} = 11.36$; $\gamma_{2'}^{\infty} = 3.00$					
C_e	γ_{1*}^{∞}	γ_{2*}^{∞}	A	B	I_{PB}	I_{PH}	γ_{1*}^{∞}	γ_{2*}^{∞}	A	B	I_{PB}	I_{PH}
1.0	27.5	3.44	3.31	1.24	3.19	2.78	14.4	3.12	2.67	1.15	2.91	2.70
2.0	34.3	3.80	3.54	1.34	3.16	2.77	18.0	3.23	2.89	1.17	3.00	2.73
4.0	54.4	3.88	4.00	1.36	3.43	2.83	28.5	3.52	3.35	1.26	3.17	2.78
4.4	59.4	3.94	4.09	1.37	3.45	2.83	31.2	3.56	3.44	1.27	3.20	2.78

constants according to the relationships

$$A = \ln \gamma_{1*}^{\infty} \qquad (17a)$$

$$B = \ln \gamma_{2*}^{\infty} \qquad (17b)$$

Table 1 shows results of these calculations and gives both the Brandani stability parameter I_{PB} and the Heidemann stability parameter I_{PH}. Infinite dilution activity coefficients evaluated from the Wilson equation lead to indications of solution instability for all mixtures containing lithium chloride. On the other hand, infinite dilution activity coefficients determined from the UNIQUAC equation lead to different results. The Brandani criterion shows stability for all but the mixtures of 1-propanol with 4 molal solutions, while the Heidemann criterion shows instability for the 2 and 4 molal solutions.

Experimental results described by Rousseau and Boone (1978) showed that mixtures of 1-propanol with 4 molal aqueous solutions of lithium chloride bordered on unstable behavior. Furthermore, Boone (1976) found that 1-propanol mixtures with 4.4 molal solutions separated into two phases; the mixture temperature was 88°C and total mole fraction x_{1*} was 0.20.

Figure 1 shows plots of A and the Brandani parameter I_{PB} as functions of C_e. These results indicate that 1-propanol mixtures with 2.53 molal lithium chloride solutions approach incipient instability. The composition of the mixture at which instability occurs can be estimated from an equation presented by Brandani (1975):

$$x_{1*} = \frac{Q - (1 - Q + Q^2)^{\frac{1}{2}}}{Q - 1} \qquad (18)$$

For $Q = 2.467$, which was determined from $I_{PB} = 3.02$, it was determined that $x_{1*} = 0.217$ and $x_{2*} = 0.783$. From the equations defining the pseudobinary mole fractions, $x_2 = 0.749$ and $x_3 = 0.034$.

As a more demanding test of the model described earlier, the ratios of infinite dilution activity coefficients as given by Equations (15) and (16) were determined for 1, 2, 4 and 4.4 molal solutions of lithium chloride in water with 1-propanol. The salt parameter k_s was 0.245, and the vapor pressure lowering of water by lithium chloride was estimated from the equation

$$\Delta P_2^s = 0.033\ C_e \qquad (19)$$

The quantity x_2^{∞} was determined recognizing that as $x_{1*} \rightarrow 0$, $x_{2*} \rightarrow 1.0$, where

$$x_{2*} = x_2 + x_3 \qquad (20)$$

$$x_3 = \frac{18\ C_e}{1\ 000} x_2 \qquad (21)$$

Table 2 summarizes the predictions from Equations (15) and (16). Clearly, the predicted infinite dilution activity coefficients compare well with experimentally determined values shown in Table 1. Brandani and Heidemann criteria are also shown in Table 2 and indicate stability limits similar to those evaluated from experimental results.

Figure 1 shows the results of the predictive calculations using the Brandani stability criterion with infinite dilution activity coefficients based on those determined by the UNIQUAC equation for salt free mixtures. From the plots in Figure 1, the model predicts that 1-propanol mixtures with 2.72 molal lithium chloride solutions approach incipient instability. Compositions at the point of instability are $x_{1*} = 0.212$ and $x_{2*} = 0.788$. As before, these pseudo mole fractions correspond to $x_1 = 0.212$, $x_2 = 0.751$ and $x_3 = 0.037$. These predictions vary somewhat from experimental results; if we consider what is asked of the model, the variation is not great and indicates that stability limits may be at least roughly approximated from minimal experimental data.

CONCLUSIONS AND RECOMMENDATIONS

The results of these analyses show instability of 1-propanol-water-lithium chloride solutions, the model of Rousseau and Boone (1978) to be useful in predicting the onset of solution instability and conditions at which the instability occurs, and that the empirical Brandani criterion (1974) correlates better with experimental data than the rigorous criterion of Heidemann (1975).

NOTATION

A, B = van Laar constants
a_i = activity of i
C_e = salt concentration in water, molality
g = specific Gibbs free energy
I_{PB} = Brandani criterion, Equation (13)
I_{PH} = Heidemann criterion, Equation (14)
k_s = salt parameter
P = system pressure
P_i^s = vapor pressure of i
Q = ratio of van Laar constants, A/B
R = gas constant
T = system temperature
x_{1*} = x_1
x_{2*} = $x_2 + x_3$
x_1 = mole fraction of salted out solvent
x_2 = mole fraction of salted in solvent
x_3 = salt mole fraction
ΔP_2^s = vapor pressure lowering of 2
γ_i = activity coefficient of i
γ_i^{∞} = infinite dilution activity coefficient of i

Superscripts

* = pseudobinary component
' = pure component

LITERATURE CITED

Abrams, D. S., and J. M. Prausnitz, "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Gibbs Energy of Partly or Completely Miscible Systems," *AIChE J.*, **21**, 116 (1975).

Boone, J. E., R. W. Rousseau, and E. M. Schoenborn, "The Correlation of Vapor-Liquid Equilibrium Data for Salt-Containing Systems," *Adv. Chem. Ser.*, **155**, 36 (1976).

Brandani, V., "Use of Infinite-Dilution Activity Coefficients for Predicting Azeotrope Formation at Constant Temperature and Partial Miscibility in Binary Liquid Mixtures, *Ind. Eng. Chem. Fundamentals*, **13**, 154 (1974).

Brandani, V., "Use of Infinite-Dilution Activity Coefficients for Predicting Azeotrope Formation at Constant Temperature and Partial Miscibility in Binary Liquid Mixtures," *ibid.*, 14, 73 (1975).

Heidemann, R. A., "Use of Infinite-Dilution Activity Coefficients for Predicting Azeotrope Formation at Constant Temperature and Partial Miscibility in Binary Liquid Mixtures, *ibid.*, 72 (1975).

Johnson, A. I., and W. F. Furter, "Salt Effect in Vapor-Liquid Equilibrium, Part I," *Can. J. Tech.*, 34, 413 (1957).

Johnson, A. I., and W. F. Furter, "Salt Effect in Vapor-Liquid Equilibrium, Part II," *Can. J. Chem. Eng.*, **38**, 78 (1960).

Long, F. A., and W. F. McDevit, "Activity Coefficients of Nonelectrolyte Solutes in Aqueous Salt Solutions," *Chem. Rev.*, **51**, 119 (1952).

Meranda, D., and W. F. Furter, "Salt Effects on Vapor Liquid Equilibrium: Some Anomalies," *AIChE J.*, **20**, 103 (1974).

Prausnitz, J. M., *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, Englewood Cliffs, N.J. (1969).

Rousseau, R. W., and J. E. Boone, "Vapor-Liquid Equilibrium for Salt Containing Systems: Correlation of Binary Solvent Data and Prediction of Behavior in Multicomponent Solvents," *AIChE J.*, **24**, 718 (1978).

Manuscript received August 9, 1979; revision received November 6, and accepted December 7, 1979.

Particle Chain Formation in Aerosol Filtration With Electrical Forces

KENNETH A. NIELSEN
and
JAMES C. HILL
Department of Chemical Engineering
Iowa State University
Ames, Iowa 50011

It is an experimental observation that aerosol particles captured by fibers in filters tend to form branched particle chains, called dendrites, rather than to distribute themselves evenly along the surface of the fibers (Watson, 1946; Leers, 1957; Billings, 1966; Yoshioka et al., 1969; Barot 1977). These dendrites are apparently better aerodynamic targets than the bare fibers. Models have been proposed to account for the formation of these deposits (Radushkevich, 1964; Yoshioka et al., 1969; Payatakes and Tien, 1976; Payatakes, 1976*a*, *b*, 1977), and some numerical simulations involving particle trajectories have been made to study the mechanisms by which the dendrites may be formed (Tien et al., 1977; Wang et al., 1977; Kanaoka et al., 1978). These simulations, made in a two-dimensional plane, incorporate the ideas that previously collected particles block out or shield portions of the collector from further use, and that particle interception is crucial for formation of the dendrites.

These numerical simulations that show dendrite growth in two dimensions do not consider electrical forces. It has been argued, however, that electrical forces are involved in the formation of chainlike aggregates on fibers (Billings, 1966) and on filter cloth (Frederick, 1974; Penney, 1977), although Payatakes (1976*a*) cites laboratory evidence for dendritic growth in liquid systems in the absence of long range electrostatic forces.

The simple numerical simulations described in the present note, carried out during some earlier studies of particle capture on fibers and droplets using electrical forces (Nielsen and Hill, 1976*a*, *b*; Nielsen, 1978*a*, *b*) and independent of those by Tien et al. (1977), were made to examine the formation of particle chains when electrical forces are intentionally invoked to improve particle collection efficiency. The results illustrate that a central electrical force increases the number of dendrites and the area they cover, but that short range forces between approaching particles and dendrites do not affect dendrite growth very much.

The simplest system to examine involves an attractive coulombic force between a charged circular fiber and oppositely charged spherical particle moving in a potential flow with negligible inertia according to the equation of motion (Nielsen, 1978*a*):

$$X_o = R \sin\theta\,(1-R^{-2}) + K_c\,(\theta-\pi). \qquad (1)$$

The second term in Equation (1) is the stream function for potential flow around a cylinder, X_o is the initial particle position, and K_c is the electrical force parameter or dimensionless mobility for the coulombic force, which falls off as R^{-1}. Equal sized particles ($\mathcal{R}=0.04$) were located randomly and with uniform probability along the line X_o and, following Equation (1), were subject to capture one at a time, either by the cylindrical collector or by particles previously collected, or else swept downstream. Particles are captured only in a single plane, strong particle adhesion is assumed and the primary coulombic force and local flow field are assumed to be unaffected by the dendrites.

With no electrical forces present ($K_c=0$), particles follow the flow streamlines and are captured only by interception. Since the trajectories tend to parallel the fiber surface, shadows cast by the first-captured particles prevent the fiber surface from capturing particles farther downstream. But once initiated, the dendrites, and hence collection rate, grow as a chain reaction. In the experiment for this case, only two dendrites were formed (Figure 1), each growing from one of two particles captured by the fiber. This growth mechanism is identical to that described by Tien et al. (1977).

With the coulombic force [Equation (1), $K_c \neq 0$], chain initiation can occur anywhere on the fiber surface with equal likelihood, and initially many short chains are formed (Figure 2). However, blocking or shadowing of some chains by others causes some chains to terminate and others to dominate the collection. Although net particle collection occurs at a constant rate and not as a chain reaction, individual dendrites grow at a rate proportional to the amount of particle flow not lying within particle shadows that a dendrite sweeps. As a result, deposition on the downstream half of the fiber becomes increasingly blocked as upstream dendrites grow. Under the same conditions, point particles would be deposited uniformly over the entire fiber.

In Figure 2, the effect of the dendrites on the local electrostatic force field is neglected, although in fact short range electrical forces arise between the fiber and the approaching particle. For instance, a charged particle approaching a neutral fiber polarizes the fiber and is attracted to it. This force becomes significant when the particle is on the order of one fiber radius away from the surface of the fiber. When the particle passes near a dendrite, the dendrite is similarly polarized, but with this local force extending only on the order of one particle radius away from the dendrite. Similarly, with a charged fiber some of the charge resides on the dendrites, and the otherwise radial electric field lines are distorted near them, curving in obliquely to the dendrite surface. The coulombic attraction for oppositely charged particles extends along these field lines, and the particles are locally attracted to the dendrites.

This localized force was crudely accounted for by simply expanding the effective capture radius of particles in a dendrite from 1 to 1.5 particle radii. Upon interception of the increased capture radius, approaching particles were pulled into actual contact with the capturing particle along their line of centers. The result of using this simulation of short range forces is shown

---

Kenneth A. Nielsen is with Union Carbide Corporation, P. O. Box 8361, South Charleston, West Virginia 25303.

0001-1541-80-3914-0678-$00.75. © The American Institute of Chemical Engineers, 1980.