arguments, the high and low conversion steady states are both stable, while the intermediate one is unstable.

From Figure 1 it is also clear that with $x_i\rho_i/\rho_o$ set at unity, the multiplicity region extends over the range $6.85 \times 10^{-4} < \rho_o/\tau MS < 11.48 \times 10^{-4}$ g-moles/cm²·s. When the value of $\rho_o/\tau MS$ is such that the CFSTR operates within the multiplicity region, then the ability of the reactor to attain the sought after high conversion steady state depends on the initial conditions and transient response.

In concluding, we have shown in this communication that under certain circumstances, concentration stability effects may exist when a liquid reactant is catalytically decomposed to a gas, within a CFSTR. Our ideas may also be useful in the understanding of electrochemical reactors where gases are commonly evolved in a side reaction (Sakellaropolous and Volintine, 1980).

ACKNOWLEDGMENT

The author acknowledges helpful discussion with Professor Charles N. Satterfield, and financial aid from the Department of Chemical Engineering at Massachusetts Institute of Technology.

NOTATION

M = molecular weight of reactant (H_2O_2)
r = reaction rate (g-mole H_2O_2/cm² catalyst surface area · s)
S = surface area of catalyst per unit volume of reactor (cm²/cm³ total reactant mixture)
x = weight fraction of reactant (H_2O_2)
ρ = density (g/cm³)
τ = CFSTR residence time (s)

Subscripts

i = reactor inlet
o = reactor effluent

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A Group Contribution Molecular Model of Liquids and Solutions:

II. Groups and Their Interactions in Water and Aqueous Solutions of Paraffins, Ketones, and Alcohols

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INTRODUCTION

Groups are structural units of molecules. There has been a sustained interest in the literature about group contribution to activity coefficients in solutions. This interest stems from the fact that large numbers of molecules are made up of a few groups. Group contribution models, therefore, offer the potential of making wide ranging predictions of numerous molecular systems using the properties of a few groups. Nitta, et al. (1977) developed a molecular model of group contributions for pure liquids and solutions, including heats of mixing and activity coefficients. Properties of four groups (CH_3, CH_2, CO, OH) and their interactions were reported, allowing the model to be applied to liquid paraffins, alcohols, ketones, and their solutions. The equations of the model of Nitta et al. (1977) will not be repeated here.

In this communication we report the description of water and aqueous solutions of non-electrolytes using the model of Nitta et al. (1977). Aqueous systems are characterized by strong hydrogen bonds and highly unusual non-ideal solution properties. The difficulty of their description coupled with their great practical importance present an unparalleled challenge to any molecular model.

Interactions of Water Molecules

The interactions of water molecules are represented in this model in two types: the hydrogen bonds WOH and the cavities CVT.

For each water molecule there are four hydrogen bonds: two through the molecule's "own" hydrogen atoms, and two through

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the neighbors's. Together they create an open tetrahedral structure. (See e.g. Prigogine 1957).

The non-hydrogen-bond interactions are non-specific in orientation, and are referred to as cavities in this work for the reason that they take place inside the open structure formed by the hydrogen bonds.

Table 1 presents the properties of water and its interactions that have been determined in this work. The table values here are for use in conjunction with the properties of CH_3, CH_2, CO, and OH groups reported by Nitta et al. (1977).

Water and Aqueous Solutions of Paraffins, Ketones, and Alcohols

By fitting the liquid molar volume and energy of vaporization of water at temperature from 5°C to 85°C we determine the values of Q_{CVT}, V_0^*, a, c, and the energy constants ϵ for WOH, and CVT interactions. Marquardt's (1963) nonlinear optimum seeking procedure is used to find the parameter values and the results are given in Table 1. The fitted properties are shown in Figure 1 for liquid volume and in Figure 2 for the energy. Good fitting is achieved with deviations less than 1% on the average for both properties, but no attempt is made to represent fine details such as the maximum density at 4°C.

The infinite dilution activity coefficients in water + n-paraffins mixtures are used to determine the energy constants of CH_3 (and CH_2) groups interacting with WOH and CVT. The CH_3 and CH_2 groups are considered to interact with the same energy, and the same constants apply to both. The basic data are γ^∞ of n-butane in water at 5°, 25°, and 45°C, of water in n-hexane at 30°C, and water in n-octane at 30°C. The fitted results are shown in Figure 3. The occurrence of a maximum γ^∞ for n-butane in water at about 25°C is correctly represented by the model.

To determine interactions of water with the carbonyl group of ketones, we fitted activity coefficients in water + acetone solutions at 25° and 75°C, heats of mixing of water + acetone at 25°C and water + 2-butanone at 25°C. Four new energy parameters are determined in this process: two ϵ, one σ_0, and one σ_l. The fitted results are shown in Figures 4, 5, 6, and 7. The deviations average less than 7% in activity coefficients and less than 40 Joules/mole in excess enthalpy.

Figure 8 shows the predicted activity coefficients in water + 2-butanone mixtures at 60°C. The results are comparable to Figures 4 and 5 with deviations less than 5% on the average for each system. Figure 9 shows the predicted excess enthalpy for water + 2-butanone at 60°C. The average deviation amounts 120 Joule/mole. The highly unusual heat of mixing of water + ketones solutions is displayed in the three figures, Figures 6, 7, and 9. The excess enthalpy is negative for water rich solutions, but is positive for ketone rich solutions. Increasing temperatures reduces the negative values but raises the positive values. These unusual features are correctly described by the model. The deficiency in Figure 9 is that the predicted rise in the positive excess enthalpy for ketone rich solutions is not quite as high as experimentally observed.

The excess enthalpies are sensitively dependent on the value of Q_{CVT}, and adjustment of its value is made from the pure water calculations in order to achieve the best excess enthalpy calculations. The value of Q_{CVT} in Table 1 reflects this adjustment and all calculated results are based on the final table value.

To determine interactions of water with the OH group of alcohols we fitted the model to data of activity coefficients for water + ethanol at 30° and 90°C, and excess enthalpy for water + ethanol at 25°C and water + n-propanol at 30°C. Two values of ϵ, σ_0, and σ are determined in this way, one each for WOH and for CVT. The calculated activity coefficients and excess enthalpies are shown in Figures 10, 11, 12, and 13 for comparison with the fitted data. Predicted properties are shown in Figures 14, 15, 16, and 17. The data shown in these figures were not used in the fitting procedure. The calculated activity coefficients are generally in good agreement with data with deviations of less than 7% on the average and the calculated excess enthalpy with deviations of less than 100 Joules/gmole on the average for each system.

The excess enthalpies of water + alcohols show a complex behavior similar to those of water + ketones. Solutions of water + n-propanol shown in Figure 13 serve as a good starting point of discussion. The excess enthalpy is negative in the water rich region and positive in the alcohol rich region. Replacing propanol with a lower alcohol enlarges the negative region at the expense of the positive region. This is shown in Figure 12 for ethanol and in Figure 16 for methanol. Replacing propanol with a higher alcohol enlarges the positive region at the expense of the negative. This is shown in Figure 17. Semi-quantitative agreement is obtained for all the experimentally observed unusual behaviors of excess enthalpy of water plus alcohol solutions.

Activity coefficients are quantitatively described except for extremely high activity coefficient values. The complex and unusual behavior of the heats of solution is represented.

TABLE 1. PROPERTIES OF GROUPS AND THEIR INTERACTION

	Q_{WOH}	Q_{CVT}	V_0^*(cm^3/gmole)	a(°K)	c
Water	4.00	2.06	10.48	55.0	.353

ϵ_{ij}KJ/gmole	CH_3	CH_2	CO	O	H	WOH	CVT
WOH	1.845	1.845	11.234	6.519	6.519	6.548	5.376
CVT	3.309	3.309	7.343	6.498	16.673	5.376	3.765

Group Pair		σ_0KJ/gmole	σ_lKJ/gmole
WOH	CO	.678	1.878
WOH	O	4.937	9.920
WOH	H	12.570	17.384
WOH	WOH	7.627	15.087

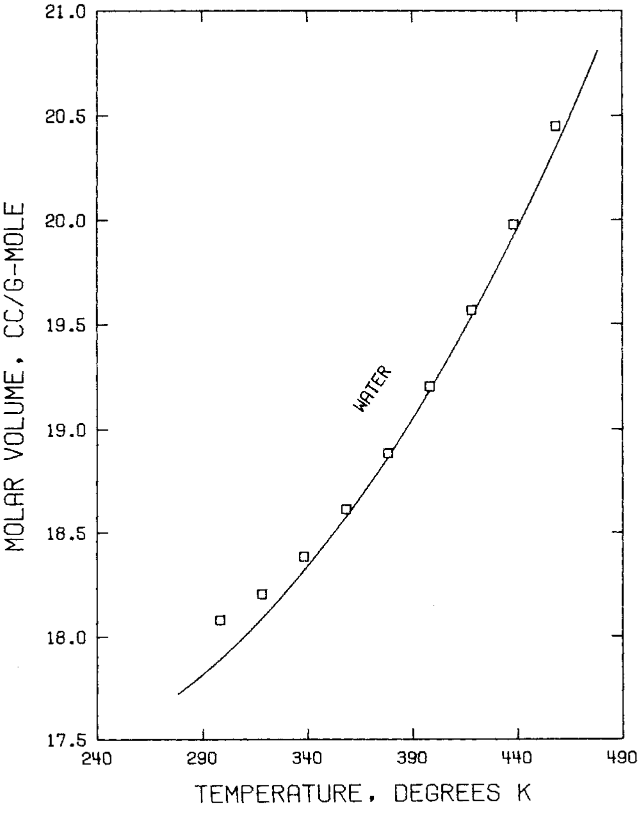

Figure 1. Molal volume of water.

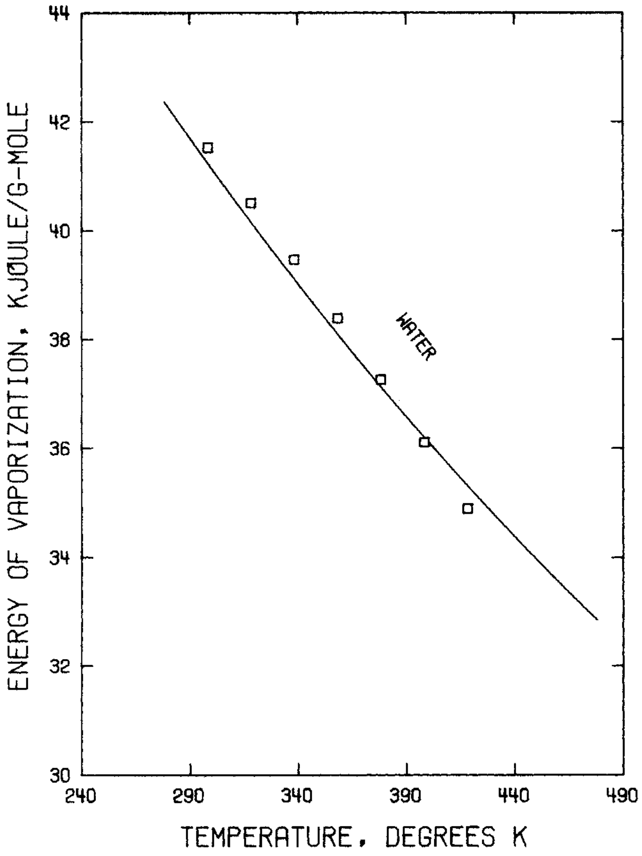

Figure 2. Energy of vaporization of water.

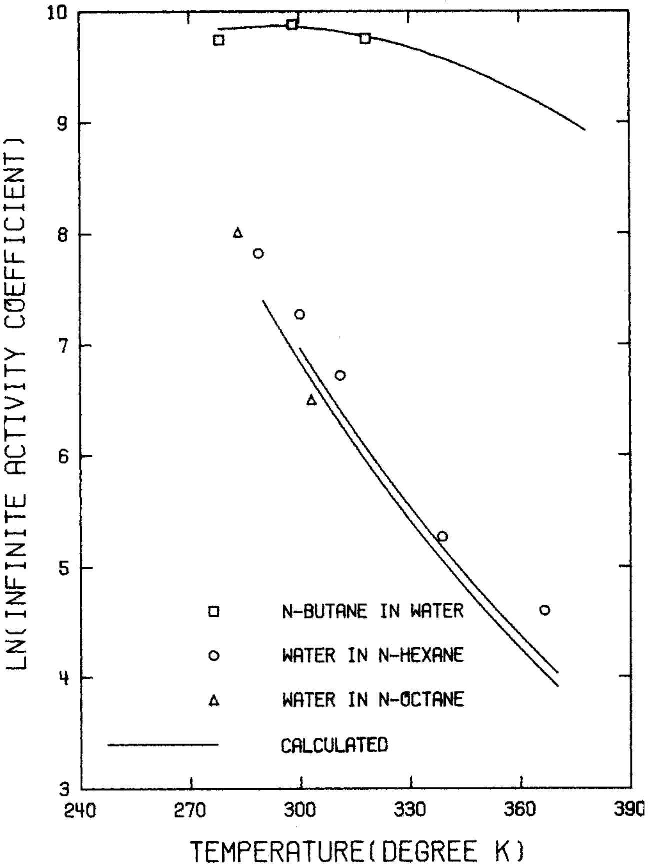

Figure 3. Infinite dilution activity coefficients of *n*-butane in water and water in *n*-paraffin as a function of temperature with data by Weflanger, Malik, and Stoller (1964) and in API Technical Data Book (1976).

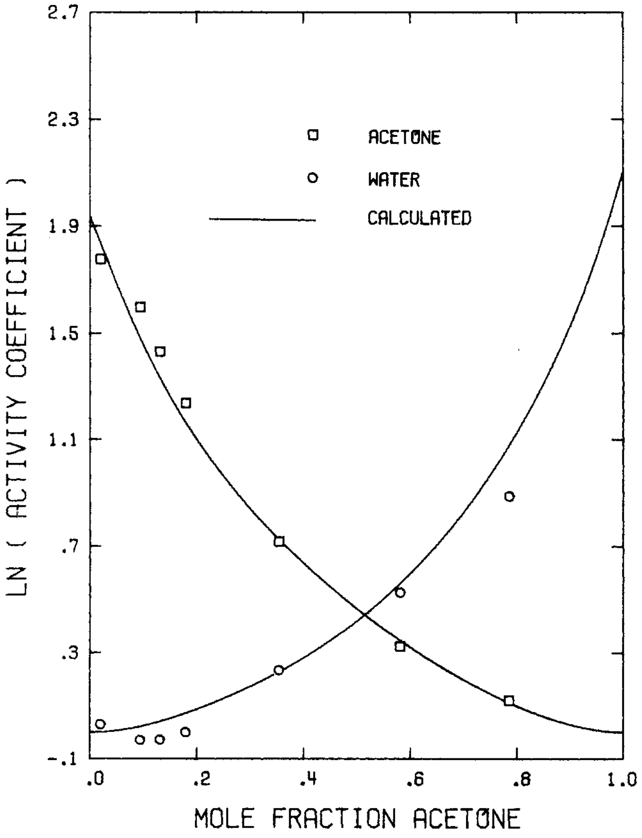

Figure 4. Activity coefficients in acetone + water at 25°C with data by Chu (1956).

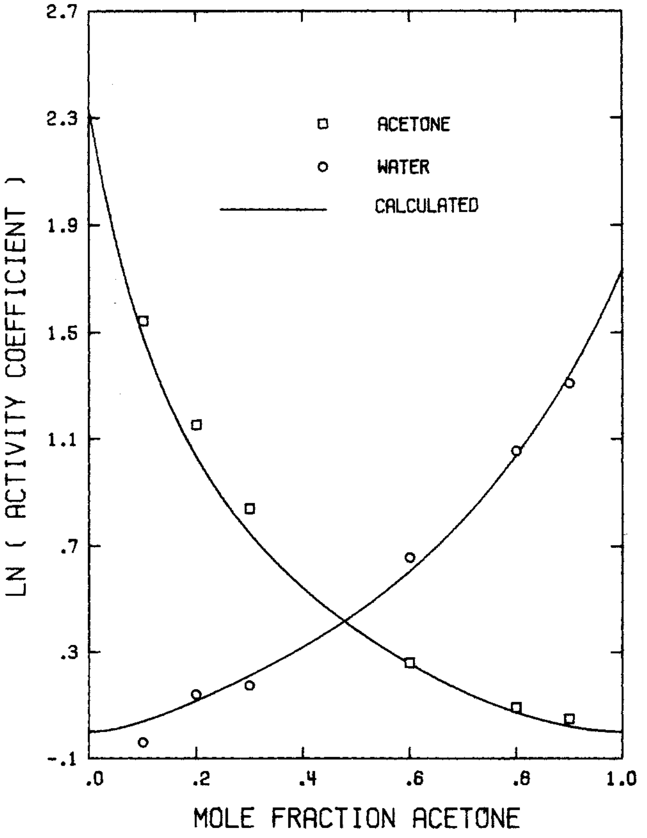

Figure 5. Activity coefficients in acetone + water at 75°C with data by Ramaiho (1971).

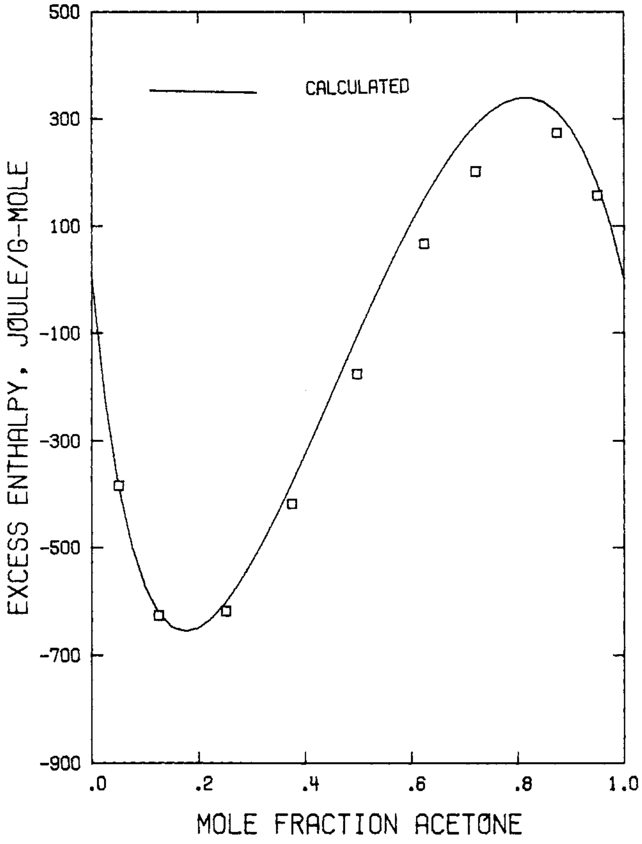

Figure 6. Excess enthalpy of acetone + water at 25°C with data of Henson, and Winkle (1960).

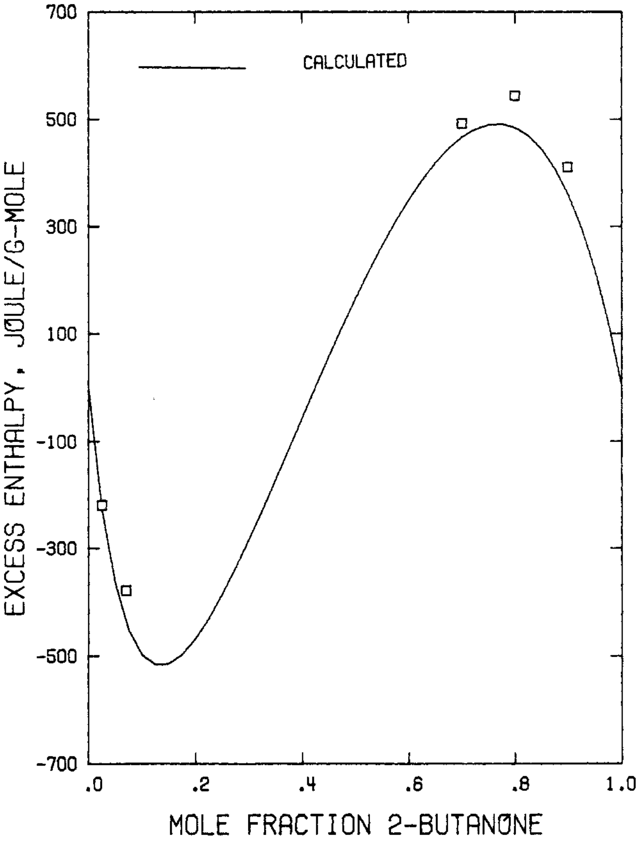

Figure 7. Excess enthalpy of 2-butanone + water at 25°C with data of Henson, and Winkle (1960).

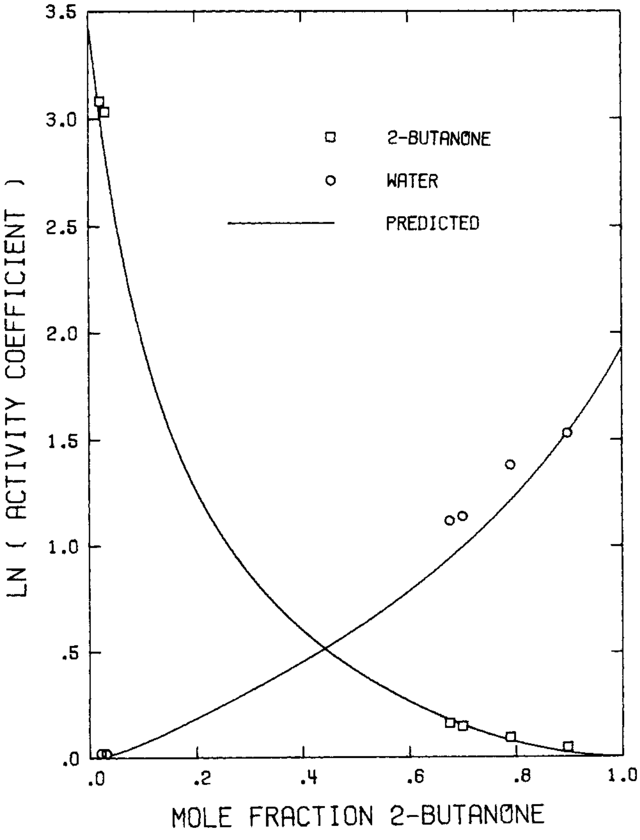

Figure 8. Activity coefficients of 2-butanone + water at 60°C with data of Altsybeeva and Morachevskii (1964).

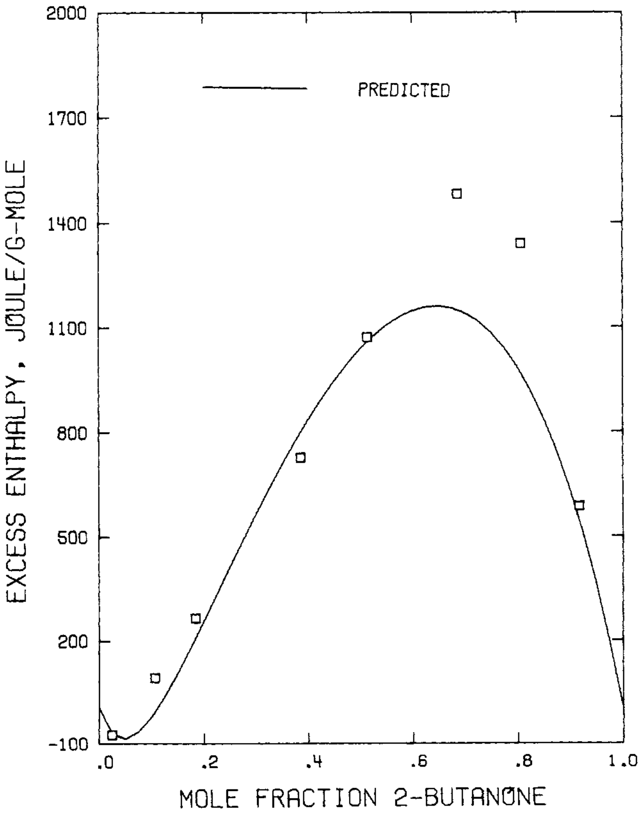

Figure 9. Excess enthalpy of 2-butanone + water at 60°C with data of Altsybeeva and Morachevskii (1964).

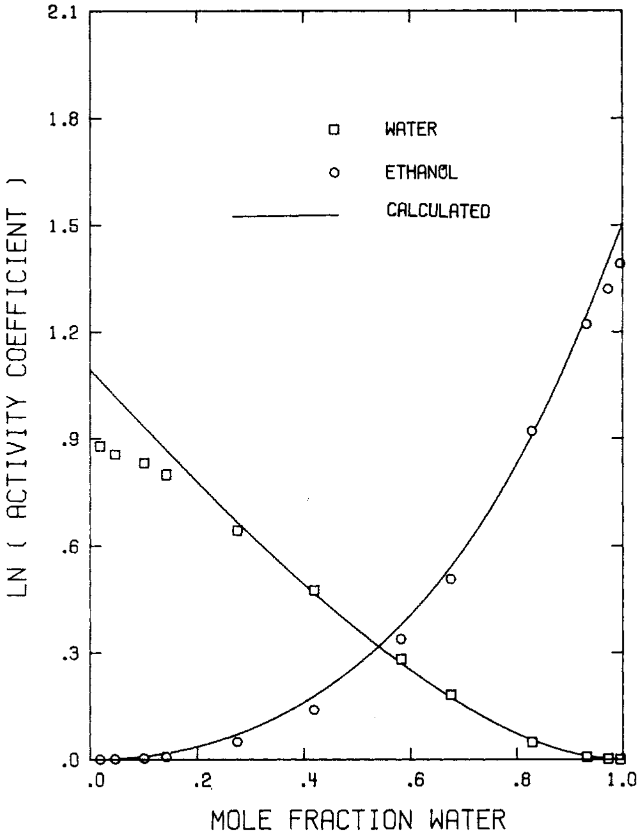

Figure 10. Activity coefficients of ethanol + water at 30°C with data of Pemberton and Mash (1978).

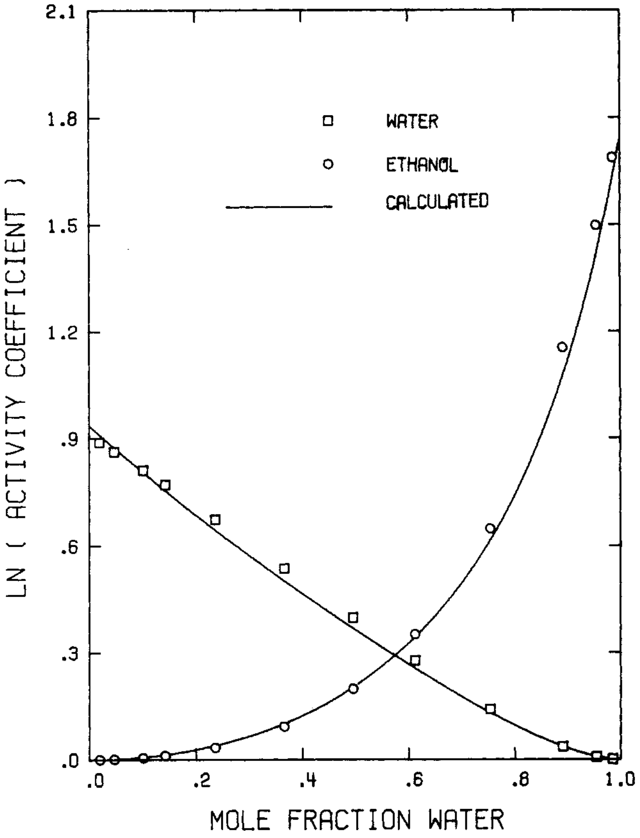

Figure 11. Activity coefficients of ethanol + water at 90°C with data of Pemberton and Mash (1978).

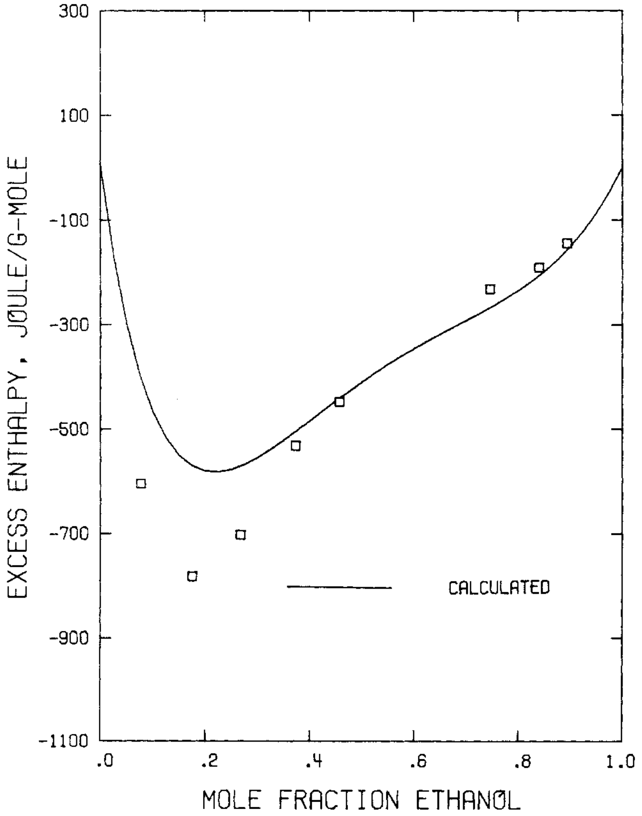

Figure 12. Excess enthalpy of ethanol + water at 25°C with data of Boyne and Williamson (1967).

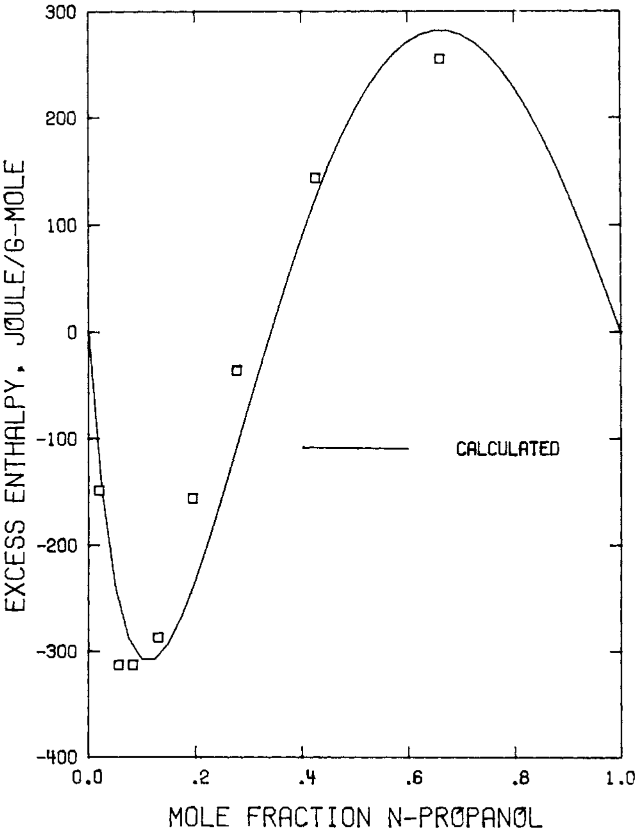

Figure 13. Excess enthalpy of *n*-propanol + water at 30°C with data of Goodwin and Newsham (1971).

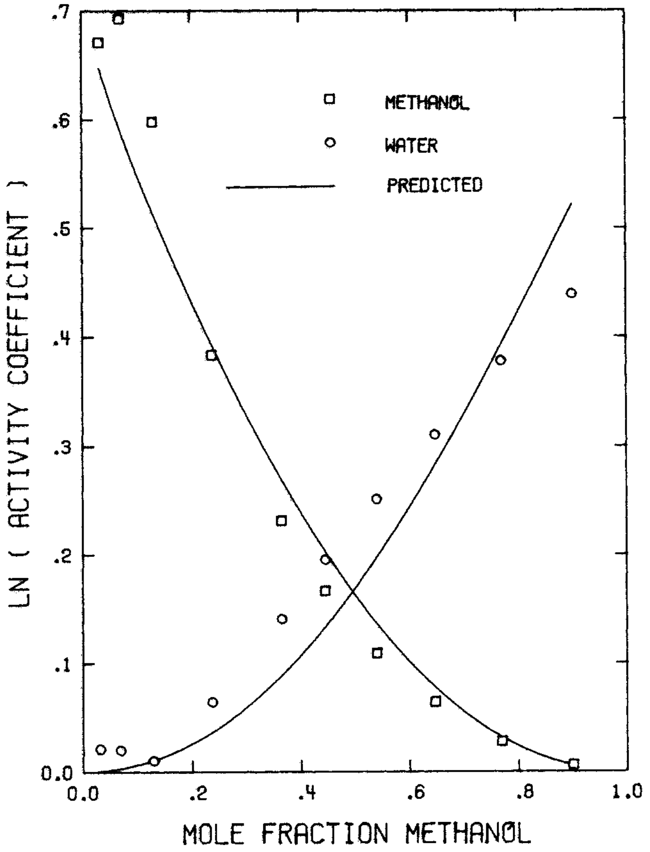

Figure 14. Activity coefficients of methanol + water at 1 atm with data of Kato, et al. (1970).

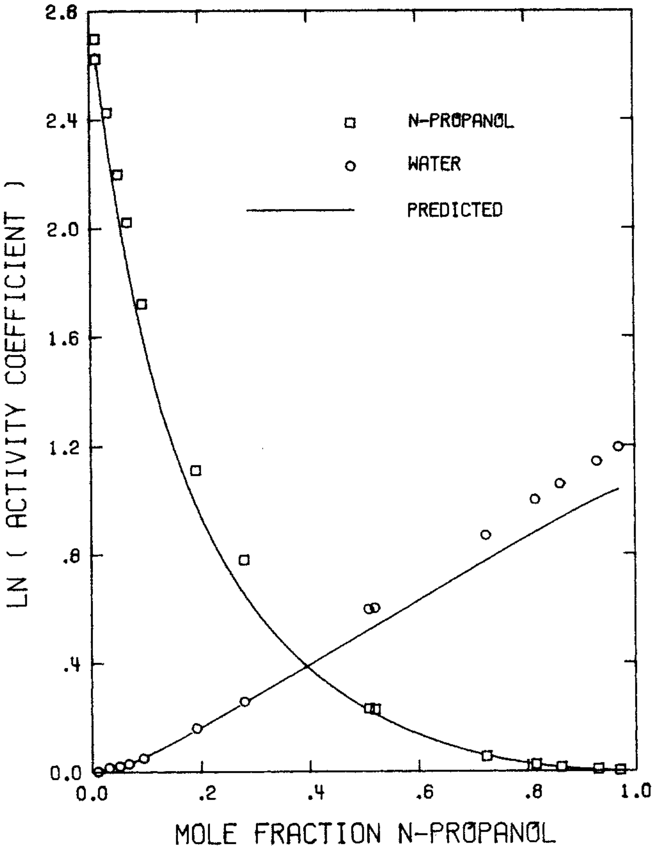

Figure 15. Activity coefficients of *n*-propanol + water at 1 atm with data of Ellis and Thwaites (1955).

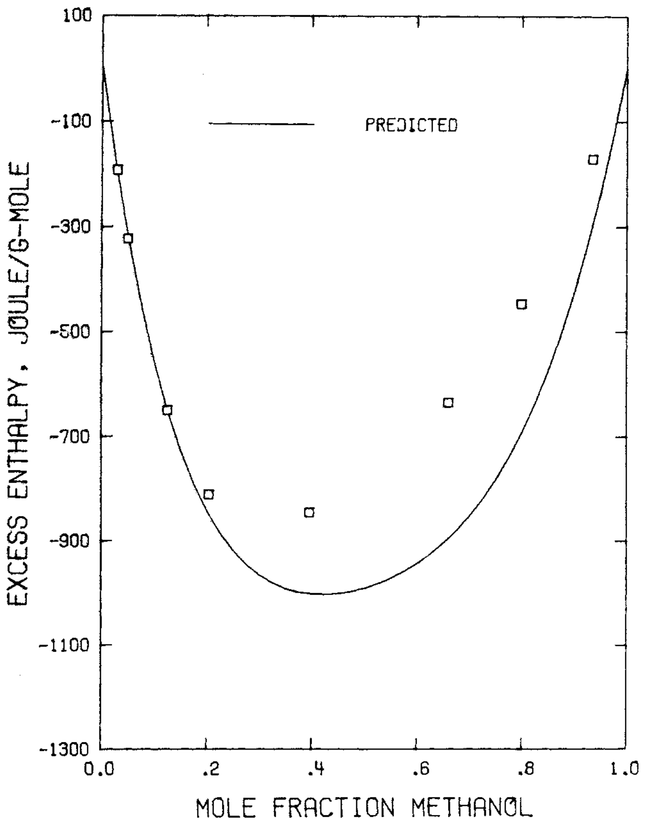

Figure 16. Excess enthalpy of methanol + water at 25°C with data of Lama and Lu (1965).

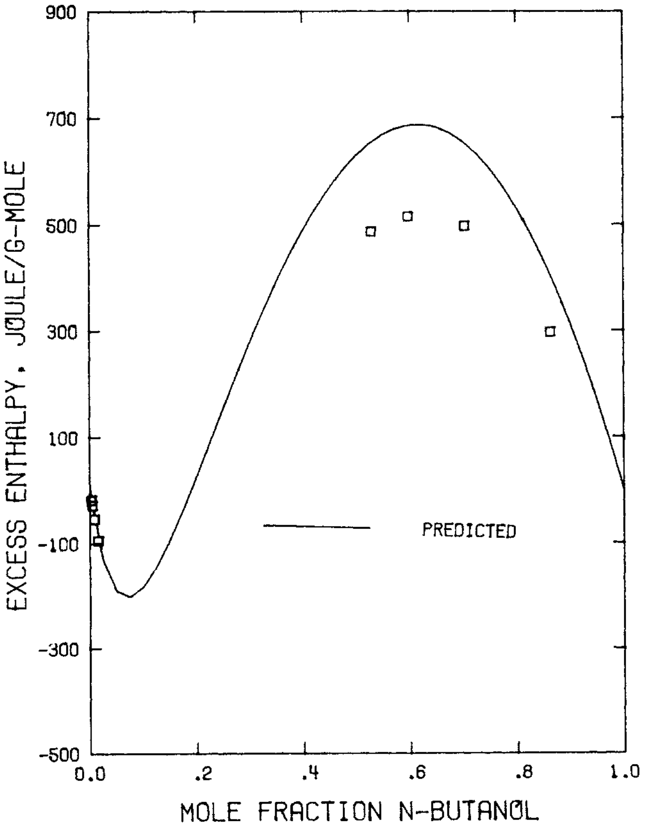

Figure 17. Excess enthalpy of *n*-butanol + water at 30°C with data by Goodwin and Newsham (1971).

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A Threshold Phenomenon in Coating Porous Surfaces with Aerosols. Applications to Antitranspirant Delivery.

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Transpiration from the leaves of plants results in enormous consumption of water supplies. The extent of irrigation needs in agriculture, and sometimes the feasibility of certain crop production in arid lands, is largely determined by this factor. Since 99% of the water which enters a plant is transpired (Gale and Hagan, 1966)—*i.e.*, only 1% is retained to sustain the life processes—there is abundant incentive to seek methods of reducing this loss. Unlike many other water "losses" in agriculture, transpiration of water to the air is irrecoverable in a given area and season. Therefore, in arid and semi-arid areas with limited water supplies, efficient and cheap methods of reducing transpiration (preferably with minimal impact on CO_2 and O_2 exchange) are important. This is particularly true when projected water demands can exceed current supplies in many regions of the world.

Extensive experimentation has been conducted with antitranspirants (*AT's*) to suppress passage of water vapor through stomata to conserve water (Waggoner and Turner, 1971; Davenport, *et al.*, 1976) and improve plant water potential (Davenport, *et al.*, 1974), although it is recognized that passage of other gases will also be affected by such methods. One of the common strategies is to occlude the stomata with a thin physical barrier to retard diffusion, and such an *AT* is usually delivered as a spray or an aerosol. Such strategies have had only limited success; the difficulty is apparently caused by incomplete coverage of the leaf surface. This is due in part to the practical problem of delivering the *AT* to leaf canopies from ground rigs or aircraft. A more fundamental problem is that spray droplets may occlude stomata directly at the impact point, but since spreading apparently does not occur many stomata remain exposed (Fisher and Lyon, 1972).

To facilitate rapid screening of *AT's* being designed for better spreading, a simple model system was constructed to simulate many features of the gas-exchange performance of real stomata (Erickson, 1978). The porous polycarbonate membranes made by Nuclepore Corp. (Pleasanton, CA) have uniform cyclindrical pores of suitable dimensions. Membranes selected for this study had nominal pore diameters d = 0.8, 5, 10 μm, with lengths 10, 10, 8 μm and pore (void) fractions 0.151, 0.078, 0.078 respectively. Each membrane was mounted in a glass cell and tested for either water vapor transport in a stagnant environment (Figure 1a) or for CO_2 or O_2 transport in a flowing-gas environment (Figure 1b). The CO_2/O_2 study is a significant advance over most previous *AT* investigations, which have usually been limited to measurements of water transport only.

Membranes were tested both with and without coatings. Coatings of various liquids were applied by aerosol deposition in a large flow-through chamber fed continuously by a DeVilbiss nebulizer. Silicones—chosen because of promising results with actual plants (Angus and Bielorai, 1965)—and a pure vegetable oil (*VO*) consisting of soybean and cottonseed oils, were deposited by this technique. A commercial *AT*, Wilt Pruf from Nursery Specialty Products (Greenwich, CT) was also used but the nebulizer was less effective, and a hand-operated plant mister and multiple applications were required to obtain deposition of films comparable to the 20 cs-silicone and *VO* used in most of this work.

Aerosol particle sizes were quite uniform, the number-distribution having a sharp maximum at 1.1 μm as measured with a Climet optical analyzer. Except for Wilt Pruf coating, membranes remained in the settling chamber until the desired degree of deposition D (in kg/m^2 of membrane area) had occurred, as determined by weighing. Membranes of known D were then loaded into test cells and evaluated for H_2O, CO_2, and O_2 transmission. For the uncoated case (D = 0), a special set of

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