

Application of the Solubility Parameter Concept to the Design of
Chemiresistor Arrays

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Abstract

Arrays of unheated chemically sensitive resistors (chemiresistors) can serve as extremely small, low-power-consumption sensors with simple read-out electronics. We report here results on carbon-loaded polymer composites, as well as polymeric ionic conductors, as chemiresistor sensors. We use the solubility parameter concept to understand and categorize the chemiresistor responses and, in particular, we compare chemiresistors fabricated from polyisobutylene (PIB) to results from PIB-coated acoustic wave sensors. One goal is to examine the possibility that a small number of diverse chemiresistors can sense all possible solvents—the “Universal Solvent Sensor Array”.

keywords: chemiresistor, solubility parameter, chemical sensor

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Introduction Microsensor development for sensing vapors has often focused on creating single devices or arrays with the maximum selectivity to specific vapors [1-4]. Applications include systems for environmental monitoring, industrial process control, contraband detection, etc. A problem having different constraints is the detection of solvent spills in areas containing electrical equipment: many different solvents may attack the insulators used in cables, connectors, wire bundles, and encapsulation, and the identity of the solvent is less important than its effect. Since the nature of this challenge depends on a range of unpredictable factors, good design dictates the development of a system using the minimum number of sensors capable of responding to all possible solvents. In addressing this problem, we sought to design a series of chemiresistors, whose responses span "all solvent space," and that would be planar, extremely small, and compatible with silicon microelectronics. With today's miniaturized communications technology, it is possible to envisage extremely small packages that include the sensors, analog electronics, and telemetry for transmission of sensor data. A preliminary report of this work was given at the 1998 Hilton Head Workshop [5].

Solubility Parameters. In considering the problem described above and discussing "solvent space", it is important to have a quantitative measure of solvent behavior. There are a variety of such measures. Examples of more simple concepts include the octanol/water partition coefficient, "Log P", and the solubility parameter, δ , first described by Hildebrand [6]. Both of these parameters can be determined by simple experiments, readily computed, or found in tables in the literature [7]. Here we will

describe "solvent space" in terms of δ ; the δ values for virtually all solvents fall in the range between that of isooctane (15) and water (48 in units of $\text{MPa}^{1/2}$) [7].

The solubility parameter, δ , for a given solvent (or polymer) is loosely related to the cohesive energy and thus the attractive strength among the molecules of the material. It was originally conceived to describe the free energy of mixing of non-polar, non-associating fluids, but has been extended to other solvents and to polymers. By definition, two solvents that have close to the same value of δ form ideal solutions and have almost zero heat (enthalpy) of mixing; the interactions between such pairs of solvents are physical, not chemical, in nature. An ideal solution of two liquids follows Raoult's law: in the vapor phase equilibrated with the liquid mixture, the vapor pressure of each of the solvents is proportional to the mole fraction of the solvent in the liquid phase. This is an important principle, since sensor response depends on the partitioning of vapor (i.e. the solvent) into the solid sensor-material phase, which is often a polymer thin film. Thus, the relationship between the partial pressure of the solvent vapor and the amount partitioned into the sensor film defines the sensor response. Two solvents that have significantly different solubility parameters typically do not form ideal solutions, and their heat of mixing is usually endothermic. They do not form ideal solutions, usually leading to positive deviations from Raoult's Law. That is, a larger partial pressure of one solvent is required to dissolve a given amount of it into the other solvent than if the mixtures were ideal.

The same considerations hold true for solvents absorbed by polymers, even though the polymers themselves have essentially zero vapor pressure. The well-known

Flory-Huggins theory of swelling phenomena posits that a solvent and a long-chain polymer with the same solubility parameters will show only minor deviations from Raoult's Law: about two times as much vapor pressure of the solvent is required for a given volume fraction as the simple Raoult's Law prediction. The factor of two is due to the statistical complications of the polymer chain (i.e. the monomer units of the polymer can not move as freely as the solvent molecules) [8]. If the solubility parameter of the solvent is either larger or smaller than that of the polymer, then still more solvent vapor pressure will be required to get a given volume fraction of the solvent to be absorbed by the polymer.

When the interactions between a polymer and a solvent are not exclusively physical—when chemical interactions play a significant role—the heat of mixing of the solvent and the polymer is exothermic, leading to comparatively high solubility of the solvent in the polymer, even at low partial pressures of the solvent. In such cases, however, the solubility parameter concept is completely inappropriate, because the underlying thermodynamic assumptions are predicated upon zero or endothermic heats of mixing—those situations in which interactions between the two substances are exclusively physical [7]. Exothermic dissolution of solvent in polymer leads to negative deviations from Raoult's Law. It also can result in a sensor with very high sensitivity to the solvent, but in some cases at a cost of slow reversibility. Studies of the temperature dependence of the sensor response can help determine whether the heat of mixing is endothermic or exothermic.

In addition to being able to assign values of δ for each solvent, it is also possible to assign δ values to each polymer. Polymers with a given value of δ are, in general, most readily swollen and dissolved by solvents having a similar value of δ . There are large tables of the values of the solubility parameters for both solvents and polymers in handbooks, notably ref. 7.

Sensor Arrays. There is a wide choice of possible chemiresistor systems that might be employed in the development of a sensing array for solvent spills. Among these are both ionic and electronic conducting polymers (pure polymer phases, as well as those with plasticizer added), plasticized polymers containing organic salts, and conductive-particle-loaded polymer composites. We have chosen to focus on (1) thin films of carbon-loaded (nonconductive) polymer composites and (2) thin films of ion conductors that change their ionic conductivity in the presence of analytes. Our working hypothesis is that a relatively small number of sensor materials, with widely varying solubility parameters, will be sufficient to detect the presence of all solvents.

Conductive Particle-Loaded Polymer Composites. There is a long history in the literature of polymer/conductive particle composites that can be formed as conductive, flexible films. Commercial products using this technology include resettable fuses and self-regulating heating tapes that exploit the positive temperature coefficient of resistance (PTC) property of these materials[9]. Many papers have also been published on the chemical sensing properties of these films [2, 10, 11]. The temperature, pressure, and chemical response of these films all depend on the same physics: the film resistance is a strong function of the volume fraction occupied by the conductive particles. If the

polymer host matrix increases its volume by thermal expansion, or swelling by absorbing analyte molecules, the resistance increases due to a breaking of some of the conductive pathways through the film. Intense discussion of the microscopic mechanistic details of this percolation problem continues, but the basic phenomenon produces very large changes in resistance if the polymer volume is changed close to the percolation threshold, which is usually between 20 and 40% by volume of the conductive particles. The magnitude of response of sensors fabricated in this way appears to depend almost entirely on the solvent/polymer interactions, with the metal particles serving to report the degree of swelling of the host polymer matrix.

Ionic Conductors. It has been reported in many papers that the ionic conductivity of thin films can be affected by solvents, particularly water [2]. In the case of analytes that can dissociate into ions, notably water, the new ions created by analyte absorption may cause an increase in ion concentration. In most cases, ions are already present in the sensor film and the analyte serves to increase the ionic mobility [12,13,14]. The increased mobility can be due to reduced viscosity in the polymer matrix when the analyte plasticizes the polymer, improved solvation (hence mobility) of the ionic charge carriers, or dielectric screening of the charged polymer backbone by the analyte molecules [13].

The measurement of frequency-dependent complex impedance (magnitude and phase angle) is a powerful tool to help understand the nature of analyte-induced conductivity changes in ionically conductive polymers. Sensors based on such materials do not yield meaningful information from a DC resistance measurement, because electrode polarization causes interminable drift in the response. The useful range of

frequencies may be limited at the low end by polarization effects and at the high end by capacitive shorting between measurement electrodes, or through an insulator layer and underlying substrate in the case of a dielectric-coated silicon substrate. Usually, a relatively low frequency can be found that yields reliable sensor response to a number of analytes without polarization effects. Compared to simple DC resistance, these AC impedance measurements may present a greater challenge for measurement circuit design.

Experimental Details

Measurement platforms. Interdigitated electrodes (IDEs) were fabricated at Sandia and consisted of quartz platforms (5 x 8 mm) with evaporated patterns of 50 pairs of photolithographically defined interdigitated electrodes (3 μm x 2 mm) made of 150Å chromium covered by 2000Å of gold. Spacing between electrodes was 8 μm . A widely spaced pair of electrodes (3 mm separation) was also included on the same chip, providing higher resistances for those sample materials with exceptionally low resistance across the IDEs.

Conductive Particle-Loaded Polymer Composites. Polymers used in this study were purchased from either Polysciences, Inc. (Warrington, PA), Aldrich Chemical Company (Milwaukee, WI), or Scientific Polymer Products, Inc. (Ontario, NY), and used as received. The materials include poly(isobutylene) (PIB; Cat. #18,145-5, Lot #14330DY); poly(butadiene, 1,2-syndiotactic) (PBS; Cat. #16317, Lot #23807); poly(vinyl alcohol), 88 mole percent hydrolyzed (PVA88; Cat. #02975, Lot #413323);

poly(ethylene-vinyl acetate) (PEVA; Cat. #02309, Lot #94654); and poly(diphenoxyphosphazene) (DPPZ; Cat. #421, Lot #3). The conductive colloidal particles used to form the composites were graphitized carbon (Polysciences, Inc. Warrington, PA; 27 – 30 nm). All polymers were dissolved using either deionized, distilled water, chlorobenzene, or chloroform.

Fabrication of the composite films involved adding 30 or 40% by weight of conductive carbon to the undissolved polymer in 5 mL volumetric flasks for a total “dry” weight of 0.100g (± 0.010 g). Carbon-loaded polymer samples are designated with a label “-40-C”, where the number represents the weight percent carbon. The polymers were dissolved to obtain 2%-by-volume solutions. To aid in distribution of the carbon colloidal particles, point ultrasonic (Heat Systems-Ultrasonics, Inc., Model W-385) was utilized at 15 half-second pulses with one second rest between pulses. After mixing, the finely dispersed composite solutions were filtered using a 5 μm pore-size filter. Not all composite solutions dispersed well enough to be filtered using a 5 μm filter; for these composite solutions, the filtration step was bypassed. Composite films were then either spin cast or evaporated from a drop of solution onto quartz substrates, the films fully covering the interdigitated electrodes. Spin casting was performed at 3000 rpm for 30 seconds to yield an approximately 2000 Å-thick film. Films produced from drops were allowed to evaporate to dryness on the substrates. Composite solutions with large (>75 μm) aggregates of carbon particles were drop deposited on the wider spaced electrodes to avoid shorting. Preliminary impedance screening of the coated substrates was performed using a two-point resistance probe (four point resistance measurements of these materials

will be reported in another publication). Samples that were electrically shorted or yielded low resistance ($\sim 2 - 300 \Omega$) were rejected.

Ionic Conductors. Two types of ionic conductor material were examined. The first was a polymer/liquid crystal composite film, made by dispersing 0.3 g of the nematic liquid crystal K21 (4-cyano-4'-*n*-heptyl biphenyl, EM Laboratories) in 0.24 g of PVA (MW = 25,000) dissolved in 2 – 3 mL of water.. Following dispersal of the K21, 3 mg of tetraethylammonium bromide was added to increase conductivity. The resulting mixture was blended using a mixing blade attached to a Dremel™ tool. A thin film of the suspension was smeared across the IDE. In general, attempts to spin coat the IDE led to apparent separation of the K21 from the polymer. Detailed discussions of the preparation and properties of polymer-dispersed liquid crystals appear in the literature [15].

The second material was a naturally occurring clay having anionically charged sheets, between which cations can be trapped (and exchanged), conferring ionic conductivity. Sodium hectorite was used as received from NL Industries (location??). Sensor coatings were prepared by suspending the clay in an aqueous solution of colloidal gold (Unconjugated Polygold 40nm; Polysciences Inc., Warrington, PA) and spin coating or smearing a thin film on the IDE platform. It is believed that the charged Au colloidal particles replace some fraction of the native sodium ions between anionic sheets. This confers the possibility of electronic conductivity (hopping of electrons between Au particles) as well as ionic conductivity due to the remaining concentration of Na^+ ions; the Au colloids may also affect the intersheet spacing. Atomic force microscope images of

material produced by this method showed the gold particles to be well distributed throughout the clay matrix.

Analytes and Measurements. Analytes included isooctane, cyclohexane, toluene, trichloroethylene, xylene, DIMP (diisopropylmethylphosphonate), ethanol, methanol, and water. Solvents and analytes were commercially available (Fisher Chemical) and used as received, except ethanol, which was distilled immediately prior to use to remove water. In addition, binary analyte mixtures studied included isooctane and water, and ethanol and water ranging from 0 – 40 % of either water, isooctane, or ethanol.

The final IDE devices were placed in a special stainless test fixture housed in a Fisher Scientific Isotemp™ oven. This system is capable of measuring sensor responses at temperatures as high as 100°C. Spring-loaded miniature electrical contacts—“pogo pins”—provided contact with metal pads on the IDEs. Nitrogen gas from a cryogenic source was passed through gas washing bottles filled with the analytes and maintained at room temperature. Flow rates were controlled by mass-flow controllers. Resistance measurements were made by a Keithly Model 2001 Multimeter or, in the case of high-impedance (ionically conductive) devices requiring AC measurement at specific frequencies (10^7 ohms or greater) a Stanford Research Systems SR 830 DSP Lock-in Amplifier interfaced to a Keithly Model 427 current amplifier. LabVIEW software was used to set flow controllers and acquire data from the multimeters.

Results and Discussion

We studied two important polymers not previously reported in the literature of carbon/polymer composite sensors. The first of these, PIB, is a rubbery polymer that has

been utilized extensively as a chemically sensitive coating on surface acoustic wave devices [3,16]. As a consequence, there is a large body of information on the interaction of organic vapors with thin films of this polymer, including the isotherms (sensor response vs. vapor partial pressure), speed of response for both absorption and desorption, and response to mixtures of vapors.

Figure 1 shows the response of a carbon-loaded PIB film to pulses of various concentrations of *m*-xylene vapor. The sensor temperature was maintained at 32°C in the oven; the bubbler (solvent vaporizer) temperature was 22°C. The equilibrium vapor pressure of *m*-xylene at 23°C is 7 Torr. The partial pressures in the of diluted vapor are given in Figure 1 in ppm using the atmospheric lab pressure of 630 Torr.. Response and recovery are rapid, and reproducibility is good. The inset in Figure 1 expands the responses at the lowest partial pressures.

The responses in Figure 1 are similar to those reported for PIB films on acoustic wave devices, consistent with the notion that the concentration of analyte in the film determines both the magnitude of the acoustic wave device response and the swelling of the polymer matrix, the latter affecting the volume fraction occupied by the carbon particles and hence film resistance. The PIB chemiresistor responds to a variety of organic vapors having low values for δ , characteristic of nonpolar solvents and polymers.

Figure 2 shows the relative response of the PIB-coated device to seven different solvents as a function of the solubility parameter. Plotted for comparison are the relative responses of a PIB-coated acoustic wave device [16]. PIB has a δ value of 15.5 MPa^{1/2} [7], and the peak responses of both the chemiresistor and SAW data are nearby, at 17 –

18. Obtaining a large sensor response for matching δ values holds, but with broad resolution.

Table 1 lists some common solvents, their solubility parameters, and their vapor pressures at 23°C [7]. The column labeled *LogP* is the coefficient for partitioning of the molecule between water and octanol, a widely-used metric for molecular characteristics that is easily measured and correlates fairly well with solubility parameter. This quantity is also used in the “Hansch Lipophilic Parameter” model [7], in which the difference in *LogPs* between a parent compound (often a drug molecule) and a substituent derivative is catalogued.

The second important polymer system examined is polyvinyl alcohol. This polymer is readily fabricated into thin films and is expected to interact especially strongly with polar molecules (its δ value is 25.8 MPa^{1/2} [7]); as a consequence, one would expect it to respond to analytes that might not invoke a strong response from a PIB sensor. We have incorporated PVA into our sensors in two distinct ways. The first is in the form of a carbon-loaded polymer composite (40% carbon particles by volume, the composite being abbreviated PVA/40C); the second is in the form of PVA-dispersed liquid crystal doped with an organic salt to confer conductivity. The PVA/liquid crystal system is reminiscent of the multicomponent polymer electrolyte sensors recently reported by Cammann *et al.* [12]; however, it is important to recognize that the liquid crystal imparts some important properties to the sensor. First, the liquid crystal segregates into microdroplets as the composite film forms on the sensor; thus, the films are two-phase materials, and each phase can respond differently to various vapors. The potential therefore exists for

polymer-dispersed microdroplet materials to respond to a broad range of analytes and concentrations. This topic will be explored later in this paper. The second difference is that the polymer-dispersed liquid crystals are subject to electric field effects arising from the alignment of the liquid crystal. These properties are utilized in the construction of polymer-dispersed liquid crystal optical devices; however, we have not yet explored the extent to which these effects might be useful in the sensing arena

Figure 3 shows the response curve for PVA/K21 and for PVA-40-C vs. solubility parameter. The composite carbon/polymer film shows the maximum relative response for methanol ($\delta = 29.3$) and a significant response for water (relative humidity, RH). It has a weak response for analytes with lower δ values. On the other hand, the two-phase PVA/K21 has response for analytes with both high and low δ values. The responses for the PVA/K21 were measured using a 2-Hz perturbation with a peak-to-peak amplitude of 0.5 volt using the lock-in amplifier, as described in the Experimental section. Impedance-vs.-frequency curves were similar to those obtained from poly(hexane viologen) films, which we have reported on previously [13]. The responses are also extremely non-linear, as shown in Fig. 4 by an impedance-vs.-concentration plot for several analytes. The very high sensor impedance is also a drawback of this type of sensor.

A thin film of hectorite clay applied to an IDE produces another type of sensor based on ion conduction, which responds rapidly and reversibly to water vapor and is essentially unresponsive to pure ethanol vapor. One of the disadvantages of this sensor is that its response seems to saturate at relatively low humidities [14]. We have discovered that when the clay is suspended in a gold sol and applied to an IDE from this suspension,

a film with improved sensor characteristics is produced which maintains significant insensitivity to organics and is sensitive to water over a relatively broad range of relative humidities. Figure 5 shows the relative response of a hectorite/gold-sol system to a number of solvents, including water, on the same solubility parameter scale as Figure 3. The measurement frequency was 1 Hz, the ac voltage was 2 volts and the sensor temperature, 22°C. The size, charge density, and mobility of the positively charged gold colloids all differ significantly from the Na⁺ ions that are initially between the sheets of the hectorite clay; whether insertion of the Au particles is accompanied by their charge neutralization, so that the concentration of cations does not actually diminish due to their presence, is unknown, nor can we rule out some contribution to conductivity from the electronic conductivity of the Au. Precisely how the many changes resulting from Au colloid insertion result in the improved sensor response is not understood at present.

Figure 6 uses the format of Figures 2 and 3 to plot the responses of three additional carbon/polymer composites: DPPZ (diphenoxy phosphazine), PEVA (polyethylene vinylacetate copolymer), and PBS (polybutadiene, syndiotactic), plus the PVA40C data described above. Some of the features in these responses cannot be predicted from solubility parameters, such as the low response of PEVA to DIMP compared with trichloroethylene, but no solvent goes unmeasured by at least one of the sensors. A common general feature of the response curves for all of the polymers is a bell-shaped dependence upon solubility parameter, with the peak being close in each case to the polymer's δ value. Although no simple theory predicts the width of the bell shape for a given polymer, the general principle followed is that the solvent/polymer pair with

the least endothermic heat of mixing (i.e., the closest match of δ values) has the largest response. More endothermic heats of mixing, corresponding to greater mismatch between polymer and solvent solubility parameters, yield smaller responses. Specific chemical interactions may be the source of responses that do not follow the order of solubility parameters, such as the DIMP response of PEVA [16]

Pattern Recognition. Having an array of sensors not only provides responses to a wide variety of solvents, it also presents an opportunity to identify particular solvents using pattern-recognition (PR) techniques. Visual-empirical region-of-influence (VERI) PR, developed at Sandia National Labs, has been used extensively by us to interpret data from acoustic wave and catalytic gate sensors [4, 17, 18]. Application of VERI PR is illustrated in Figure 7, showing the responses of three chemiresistors to four solvents in a 2-D projection of a 3-D plot. Each point represents a different concentration of the indicated solvent (the fraction of saturation vapor pressure, p/p_{sat} , ranging from 3% to 40%). The responses have been equalized and normalized so that each response is represented by a vector ending on the surface of a unit sphere (outlined by the solid curves). The reader's vision allows her/him to see that classification of the signals from each of the four solvents is unambiguous at all tested concentrations.

VERI PR can be used for large arrays (higher dimensions than three, where human visualization of 2- or 3-D representations of the data becomes difficult or impossible); it reports whether the response to an unknown sample clusters with any previously tested classes, or must be treated as a previously untested chemical.

Furthermore, VERI can select an optimal array from a large set of sensor materials, using a completely objective method to evaluate the responses from all sensors and finding the subset that produces the greatest accuracy in identifying all concentrations of all analytes examined. It is not invariably true that the addition of more sensors confers greater recognition accuracy to the array; in fact, this is the case only when each new sensor added to the array confers chemical information that is not already provided by the other members of the array. The sensors used in an array must be exposed to a fairly large number of concentrations of a wide variety of solvents in order to give accurate recognition in a field environment.

Binary mixtures. A further complication in field applications is the chance that the sensors will be exposed to mixtures of vapors; the most common would be water vapor from normal relative humidity, combined with some solvent that has been spilled. This situation requires a still larger training set with many concentrations of binary mixtures included. Our experiments have shown that, in many cases, the signals from concentrations of binary mixtures are not simply the sum of the signals from the responses to each analyte alone. Fortunately the VERI PR algorithm is not hindered by such non-linearities. The ideal case for binaries would be two sensors that are mutually orthogonal; that is, each responds only to one of the two vapors. This is almost the case for mixtures of isooctane and water, as shown in Figure 8. In this case, the plot is in the form of the responses of two sensors plotted vs. each other. One is PEVA-40-C and the other is PVA-40-C. From Figure 6, it can be seen that these two materials are a good choice if the goal is to measure independently the responses to polar vs. non-polar species

(high δ vs. low δ values). The dashed horizontal lines connect points of constant isooctane concentrations, while the data points show monotonically increasing RH. The isoconcentration lines for each chemical would be perfectly vertical and horizontal if the responses were perfectly orthogonal(that is, if the PVA sensor had no response to any concentration of isooctane and PEVA sensor had no response to any level of relative humidity). In the present case, the figure reveals that this is not quite true. In particular, note that at $p/p_{sat} = 20\%$ for isooctane, an increase in RH actually causes the PEVA signal to decrease. We rely on the pattern recognition algorithm, using several sensors, to identify such responses as belonging to a binary mixture of some concentrations of water and isooctane; the set of all possible water/isooctane mixtures is defined as a distinct chemical class by our pattern recognition method. Once the mixture has been properly classified, the actual concentrations are obtained from a plot such as that in Figure 8, taking advantage of the fact that any new pair of responses will be surrounded by four points from the training set (unless the new points fortuitously fall directly over a pair of the existing training set points). Simple interpolation then gives a reasonably accurate estimate of the individual concentrations of water and isooctane in the new sample.

Figure 9 shows an example of a more difficult case: binary mixtures of ethanol and water. The two sensors whose responses are shown here are again PEVA-40-C and PVA-40-C. PIB would have been a poor choice in this case because it has almost no response to either ethanol or water. It can be seen from the curvature of the isoconcentration lines that significant errors would result if only one sensor was used. For example, at the lower levels of ethanol concentration, the difference in the PEVA

responses for 40% RH vs. 0% RH would result in a factor of three error in the estimate of the ethanol concentration. At the higher levels of ethanol, the RH makes less difference in the concentration estimate.

In a future publication we will discuss more binary combinations and the pattern recognition schemes for identifying binary classes.

The Chemical Fuse. An interesting and valuable property of the carbon-loaded polymer composite chemiresistors is that very high concentrations of solvent cause orders-of-magnitude increase in their resistance; this is a consequence of an increase in the average spacing between carbon particles to a distance over which electron hopping is very difficult. In cases where the polymer can dissolve completely in the solvent (analyte), and if there is a source of sufficient mechanical agitation accompanying dissolution, the sensor will remain permanently at high (in some cases infinite) resistance; the sensor is destroyed. In other cases, however, the solvent will eventually evaporate in much the same way that the sensor was originally fabricated, restoring the sensor resistance to approximately its starting value.

An example of the response from a "chemical fuse" is represented by Figure 10 where a drop of liquid isooctane was placed on a horizontally-oriented PIB-based IDE sensor. The sampling period was 100 ms; in less than one second, the resistance increased more than three orders of magnitude. As long as liquid isooctane remained visible on the sensor, the resistance remained very high (300 M Ω), but measurable. As the isooctane evaporated, a sharp drop in resistance was observed. Following complete evaporation, the sensor was still functional for sensing lower concentrations, but the

baseline resistance had decreased permanently. Subsequent doses of liquid isooctane always produced large increases in resistance, but the “under-liquid” and baseline resistances changed by smaller amounts. Further engineering is required to make a reproducible fuse similar to the commercially available PTC (positive temperature coefficient) electrical fuse based upon carbon-loaded polymer [9].

Conclusions

We believe the results presented in this paper demonstrate that an extremely small, low-power-consumption array of chemiresistors can identify almost any kind of solvent spill. This preliminary report builds the framework for further efforts to develop the “Universal Solvent Sensor.”

Solubility parameters were used to characterize sensor films and as an aid in selecting sensors for use in arrays to discriminate between members of similar or dissimilar solvent classes. Chemiresistors based on several carbon-loaded polymers were studied, along with an ionically conductive, polymer-dispersed liquid crystal system, as well as an ionically conductive clay material loaded with colloidal gold particles. The various sensors show differing sensitivities in different regions of “solvent space.” PIB shows maximum sensitivity to analytes characterized by small δ values, while PVA responds best to solvents with large δ values. The PVA/K21 two-phase polymer/liquid crystal film has the broadest response range of the materials evaluated. Additional data must be acquired to provide adequate training sets for determining a range of unknowns in the field.

The feasibility of selecting 3 or 4 sensors, at least one of which responds to every possible solvent above some threshold concentration, is demonstrated. Although some solvent might produce too small a response to be detected, our logic in protecting electronic components and packaging is to select polymers representative of those used in such applications. We show how chemiresistors can act as resettable chemical fuses to give rapid, unambiguous warning of a solvent spill. The chemical fuse failure mode is high resistance, so other hazards such as fire, physical destruction, or strong oxidizing agents (e.g., nitric acid) will yield a similar failure response.

Conductive particle/polymer composite sensors can be fabricated in an extremely small ($< 1 \text{ mm}^2$) planar format and consume almost no power to measure DC resistance. Monolithic sensor arrays with a number of different coating materials are readily fabricated using automated fluid-dispensing techniques. Ionic conductivity-based sensors are equally small, but require more complex circuitry for AC measurement; unique stability, selectivity or sensitivity can make these materials attractive nonetheless.

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References

- [1] P. T. Moseley, J. O. W. Norris and D. E. Williams, Eds. *Techniques and Mechanisms in Gas Sensing* IOP Publishing (Adam Hilger Series on Sensors), Bristol, England. (1991).
- [2] G. Harsanyi, *Polymer Films in Sensor Applications*, Technomic Publishing, Lancaster, PA (USA), 1995
- [3] D.S. Ballantine, Jr., et al. *Acoustic Wave Sensors: Theory, Design and Physico-Chemical Applications*, Chap. 5, Academic Press, Inc., San Diego, CA, (1997).
- [4] G. C. Osbourn, J. W. Bartholomew, A. J. Ricco and G. C. Frye, , *Accts. Chem. Research*, **31**, 289 (1998).
- [5] R. C. Hughes, M. P. Eastman, W. G. Yelton, A. J. Ricco, S. V. Patel, and M. W. Jenkins, *Tech. Digest 1998 Solid State Sensor and Actuator Workshop* (Hilton Head, SC, June 1998), Transducers Research Foundation, Cleveland (1998), pp. 379-382.
- [6] D. W. Van Krevelen, *Properties of Polymers*, Elsevier (New York) (1976). Chapter 7
- [7] E.A. Grulke, in *Polymer Handbook* 3rd Edition, J. Brandrup and E.H. Immergut Editors. Wiley and Sons, New York, (1989), p. VII/519 also *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, A. F. M. Barton, Editor CRC Press, Boca Raton, Florida (1983).

[8] L. R. G. Treloar, *The Physics of Rubber Elasticity*, Oxford Press London, 2nd Edition, (1958), Chapter 7.

[9] M. B. Heaney, *Appl. Phys. Lett.* **69**, 2602 (1996).

[10] M. C. Lonergan, E. J. Severin, B. J. Doleman, S. A. Beaber, R. H. Grubbs and N. S. Lewis, *Chem. Mater.* **8**, 2298 (1996).

[11] B. Lundberg and B. Sundqvist, *J. Appl. Phys.* **60**, 1074 (1986)

[12] K. Cammann, K. Buhlmann, B. Schlatt, H. Muller, and A. Choulga, *Digest of Transducers, '97*, (Chicago, Ill. June 16-19, 1997) pg 1395.

[13] K. B. Pfeifer, R. C. Hughes, M. W. Jenkins, and T. W. Schneider, to be published in *J. Electrochem. Soc.*

[14] R. Venedam, M. P. Eastman, B. L. Wheeler, C. McClellan, C. Coulliette, and N. L. Eastman, *J. Electrochem. Soc.* **138**, 1709 (1991).

[15] K. S. Drzaic, *J. App. Phys.* **60**, 2142 (1986).

[16] R. A. McGill, M. H. Abraham and J. W. Grate, *Chemtech*, **Sept. 1994** pg. 27-37.

[17] G. C. Osbourn, J. W. Bartholomew, G. C. Frye, and A. J. Ricco, Technical Digest, Solid State Sensor and Actuator Workshop (Hilton Head Island, South Carolina, June 13-16, 1994) pp.193-196.

[18] A. J. Ricco, R. M. Crooks, and Gordon C. Osbourn, *Accts. Chem. Res.*, **31**, 289 (1998).

Table 1. Hildebrand solubility parameter (δ) for a number of common solvents ranked from lowest to highest from ref. [7]. The values for DIMP and DMMP (dimethylmethylphosphonate) were calculated and are not in ref. [7]. Also shown are the calculated values for the partition coefficient between water and octanol [7], frequently called " $\log P$ ", and the saturated (equilibrium) vapor pressure at 23 °C .

Solvent	Partition coeff. water/octanol	Solubility parameter	Saturation vapor pressure
	$\log P$ (calc.)	(δ , MPa ^{1/2})	p_{sat} @ 23 °C (Torr)
Isooctane	4.46	14.1	45
Cyclohexane	3.39	16.7	89
1,1,1-Trichloroethane	2.1	17.5	117
Carbon Tetrachloride	2.86	17.7	100
<i>m</i> -Xylene	3.14	18	7
Toluene	2.68	18.2	26
Benzene	2.22	18.7	83
Chloroform	1.76	18.9	178
Methyl ethyl ketone	0.37	19	90
Tetrahydrofuran	0.33	19.5	160
Chlorobenzene	2.81	19.5	10
Cyclohexanone	0.76	19.6	4
Benzaldehyde	1.64	19.7	0.8
DIMP	0.9	20	0.7 ^a
Tetrachloroethane	2.17	20	12
Acetaldehyde	-0.16	20.1	890
1,1,2-Trichloroethane	1.68	20.2	22
Trichloroethylene	2.26	20.2	68
Acetone	-0.16	20.5	212
Pyridine	0.73	21.8	18
DMMP	-0.86	22	3
Cresol	1.94	22.7	0.1
N,N-dimethylformamide	-1.01	24.9	3.3
Ethanol	-0.2	26	52
Methanol	-0.72	29.3	114
Water	-1.38	48	21

^aL. J. Kepley, R. M. Crooks, and A. J. Ricco, *Anal. Chem.*, 64, 3191 (1992).

Figure Captions

Fig. 1. Response of a chemiresistor to pulses of different concentrations of xylene in N₂. The sensor is a carbon powder-loaded (40% by volume) film of polyisobutylene (PIB) held at 32 °C in an oven-mounted test fixture. The xylene is in a bubbler held at 22°C where the saturation vapor pressure is 10,500 ppm by volume. The arrow followed by the partial pressure shows the time at which a flow with that concentration is started. The dry N₂ purge can be seen in each case by the sharp drop in resistance.. The inset shows an expanded view of the response at lower concentrations.

Fig 2. Response of the PIB sensor to a variety of solvents with the maximum signal at $p/p_{sat} = 10\%$ normalized to 1. These data are compared with the measured partition coefficients from ref. [16] for the same solvents (as well as some additional ones) and plotted vs. the solubility parameters (Table 1) of the solvents. This demonstrates that the chemiresistor response is closely related to the swelling of the polymer phase.

Fig. 3. Normalized response of the two kinds of polyvinyl alcohol (PVA)-based sensors plotted vs. solubility parameter as in Fig. 2. The two-phase polymer/liquid crystal composite, PVA/K21 (circles), has a broader response than the single-phase PVA-40-C (triangles), but requires AC voltages for measurement.

Fig. 4. PVA/K21 responses for several solvents in terms of impedance, Z , in ohms at 2 Hz, vs. the concentration in units of fraction of p_{sat} for each solvent at 21°C.

Fig. 5. A plot in the same form as Fig. 3 for a hectorite (clay)-based sensor incorporating colloidal gold particles. The normalized response is obtained from AC impedance measurements. Experimental conditions were 22°C, 1 Hz, and 2 V peak to peak excitation.

Fig. 6. Responses of five carbon/polymer composite sensors vs. solvent solubility parameter. The log scale helps to separate the responses; the "Signal-to-Noise Baseline" gives an indication of the size of signal below which data are generally unreliable due to drift and noise. The symbols identify the polymers, which are defined in the Experimental section.

Fig. 7. Pattern recognition plot for identifying individual solvents from the simultaneous response to three different sensors. Each point is for a different concentration of the labeled solvent and each axis of the 3-D plot represents the normalized response of one of the sensors. Because the three actual responses have been normalized to the largest response, each set becomes a unit vector appearing on the surface of a unit sphere for ease in viewing the data. Isooctane is the easiest to identify because it only has a significant response on the PIB sensor. Ethanol and DIMP are harder to separate using these three

sensors, but the more sophisticated pattern recognition algorithm has little difficulty classifying them.

Fig. 8. The response of two sensors to mixtures of water (relative humidity) and isooctane vapors. Each data point is from the simultaneous response of the two sensors; the data points show monotonically increasing relative humidity (0, 5, 10, 20, and 40%) and the horizontal dashed lines are isoconcentrations for isooctane with the concentrations as indicated in the figure. The individual concentrations for a new mixture can be estimated by interpolation from the isoconcentration lines shown, which constitute a training set. Additional training set data need to be taken to improve the accuracy in determining unknowns.

Fig. 9. The response of two sensors to binary mixtures of ethanol/water using the same two sensors as for the results in Figure 8. Again, the relatively horizontal dashed lines are for the different ethanol concentrations given in the figure. The monotonically increasing relative humidity corresponding to the data points is 0, 5, 10, 20 and 40%.

Fig. 10. Resistance of a PIB-40-C sensor acting as a (resettable) chemical fuse to liquid isooctane. A very rapid increase in resistance is observed upon contact of a small drop of isooctane with the sensor (data obtained at 0.1 s per point from a 16-bit digitizer); recovery results when the isooctane evaporates away.

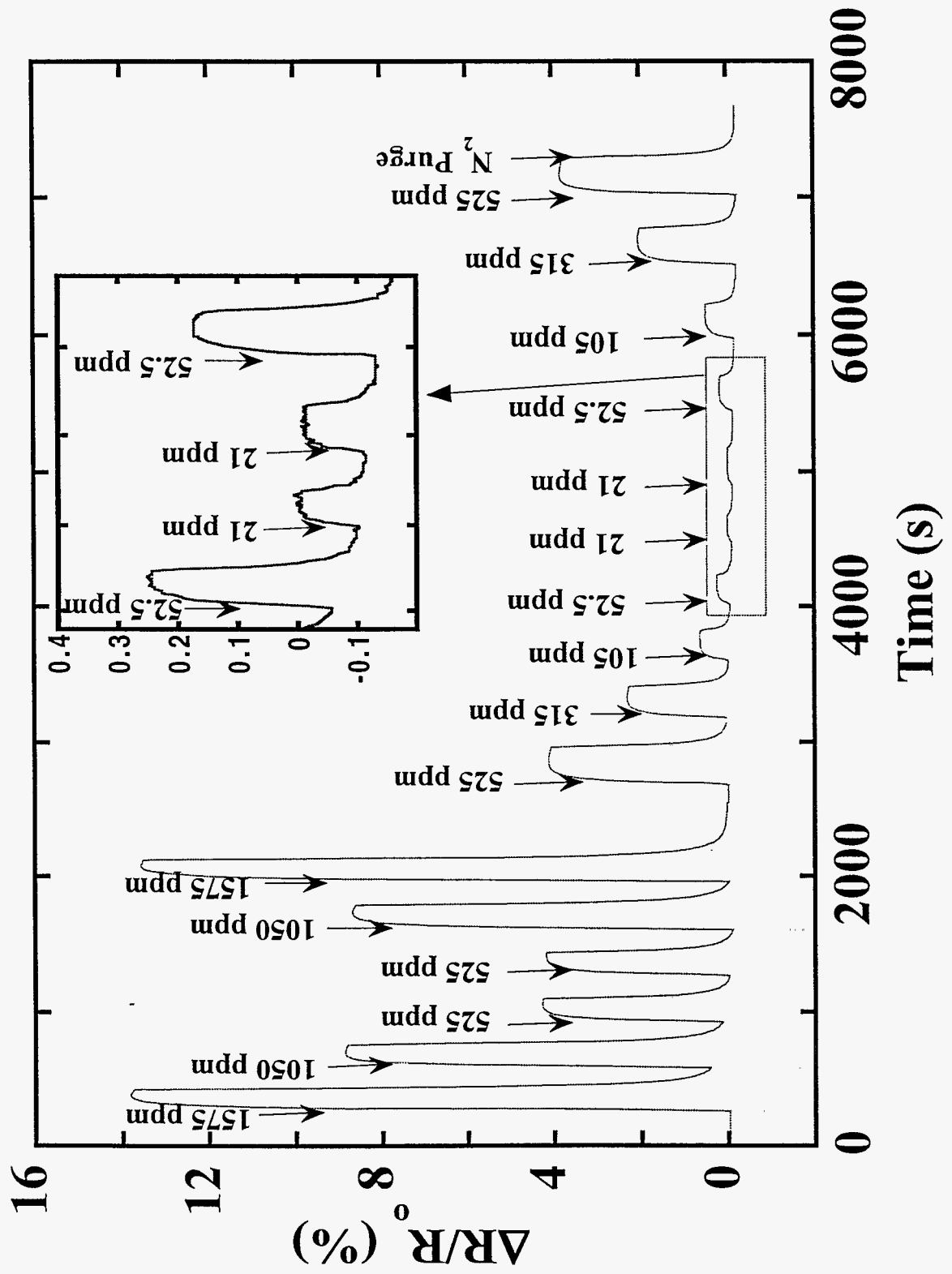


Figure 1/Eastman, et al.

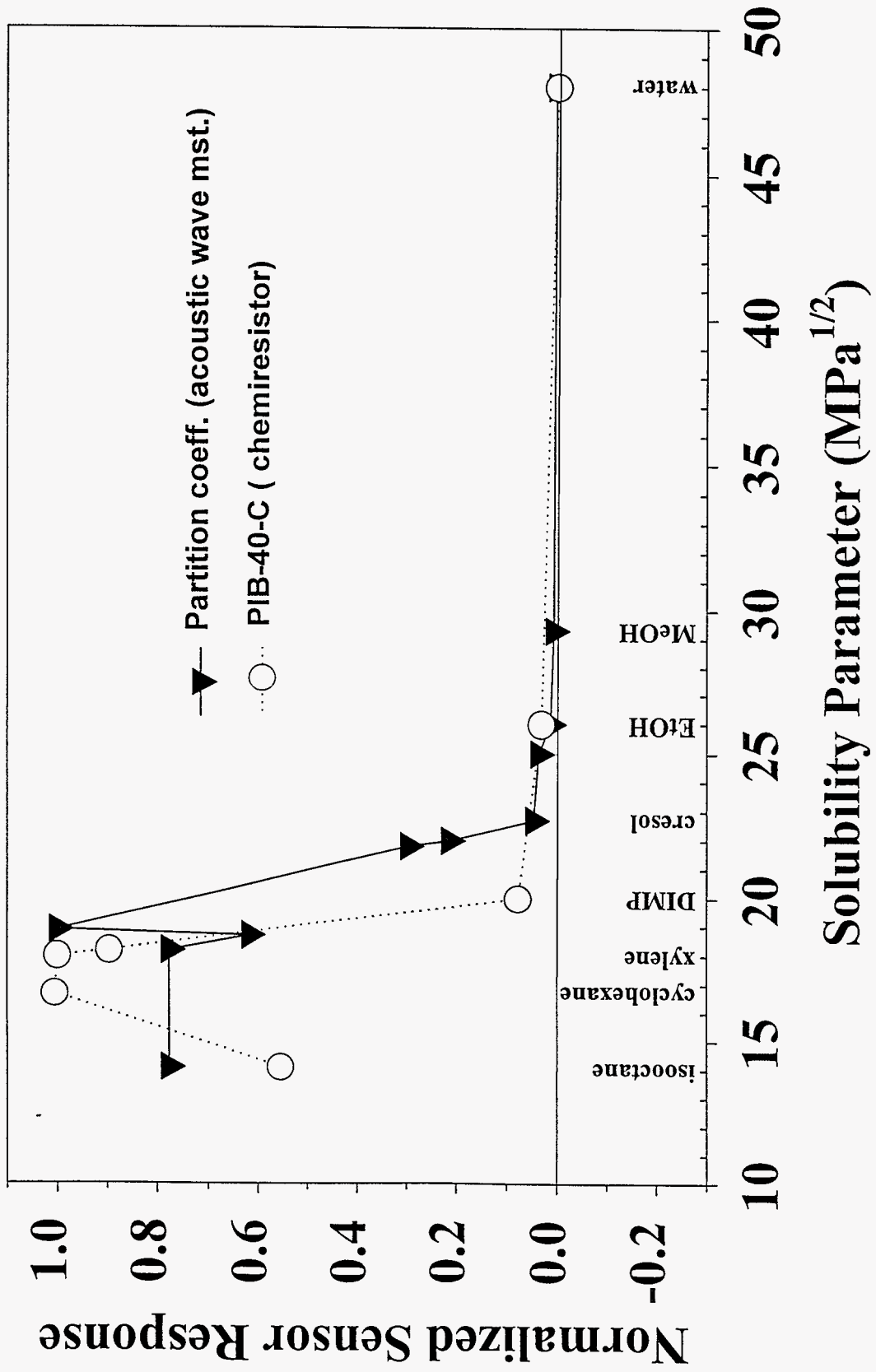


Figure 2/Eastman, et al

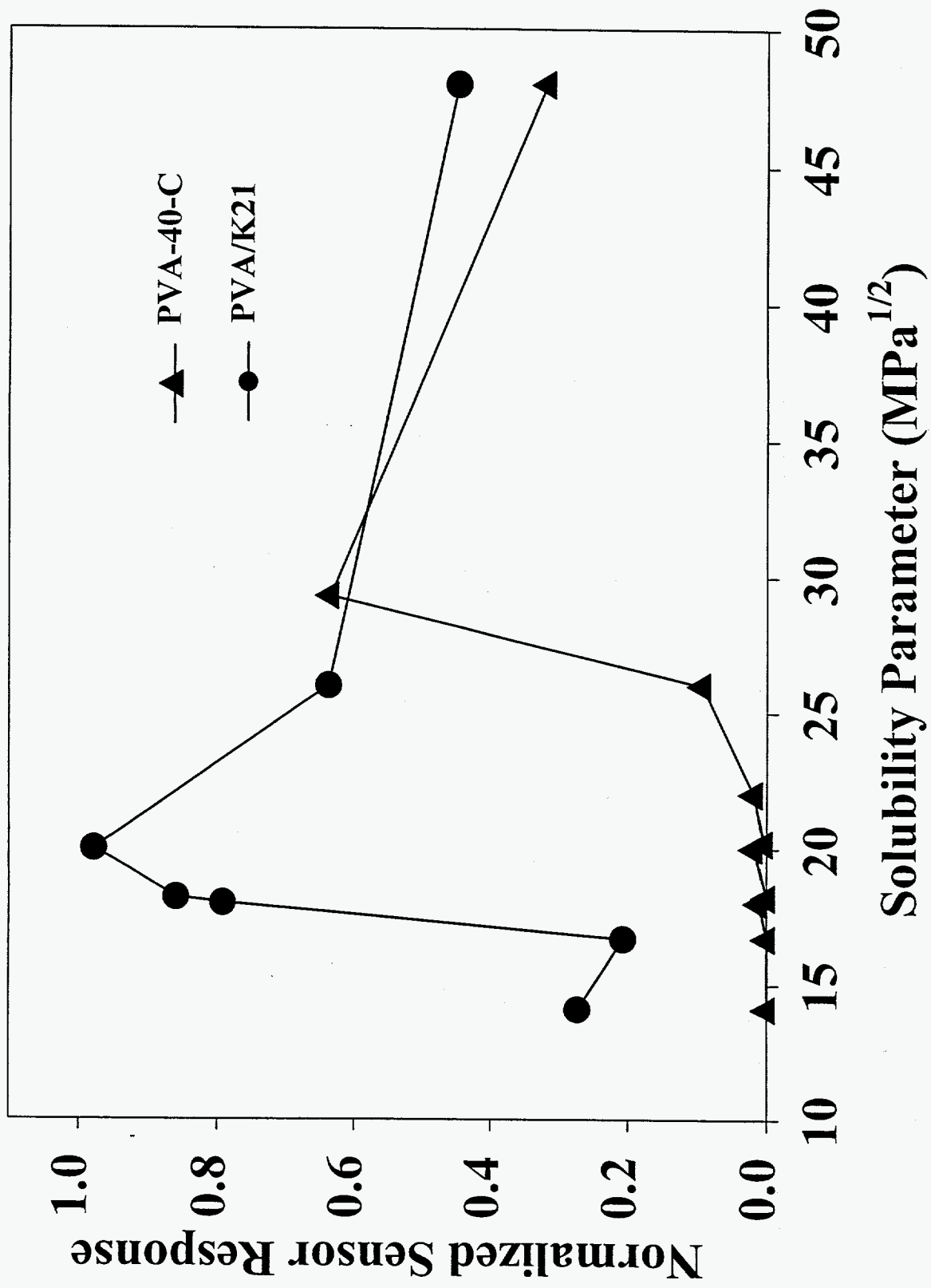


Figure 3/Eastman, et al.

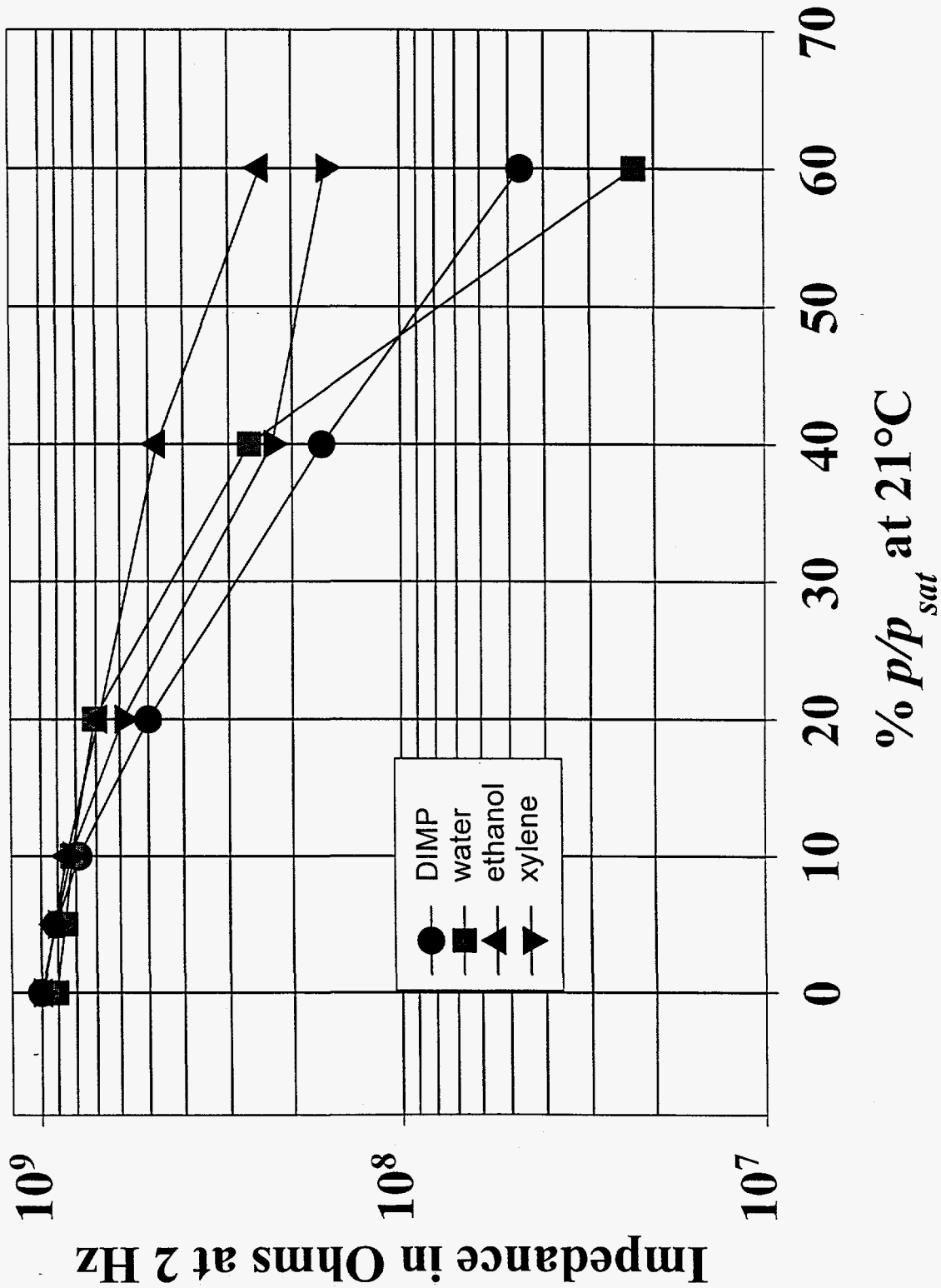


Figure 4/Eastman, et al.

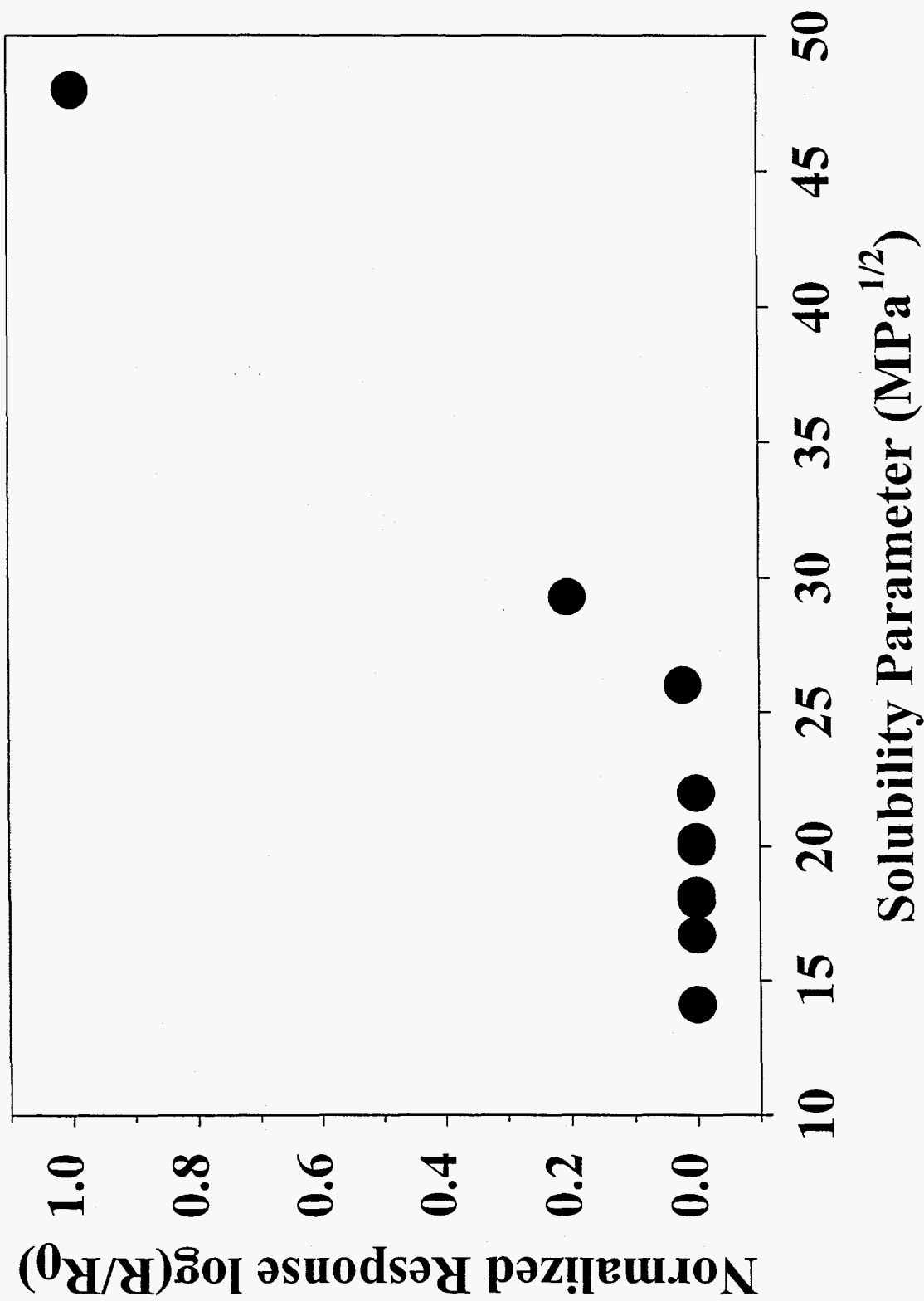


Figure 5/Eastman, et al.

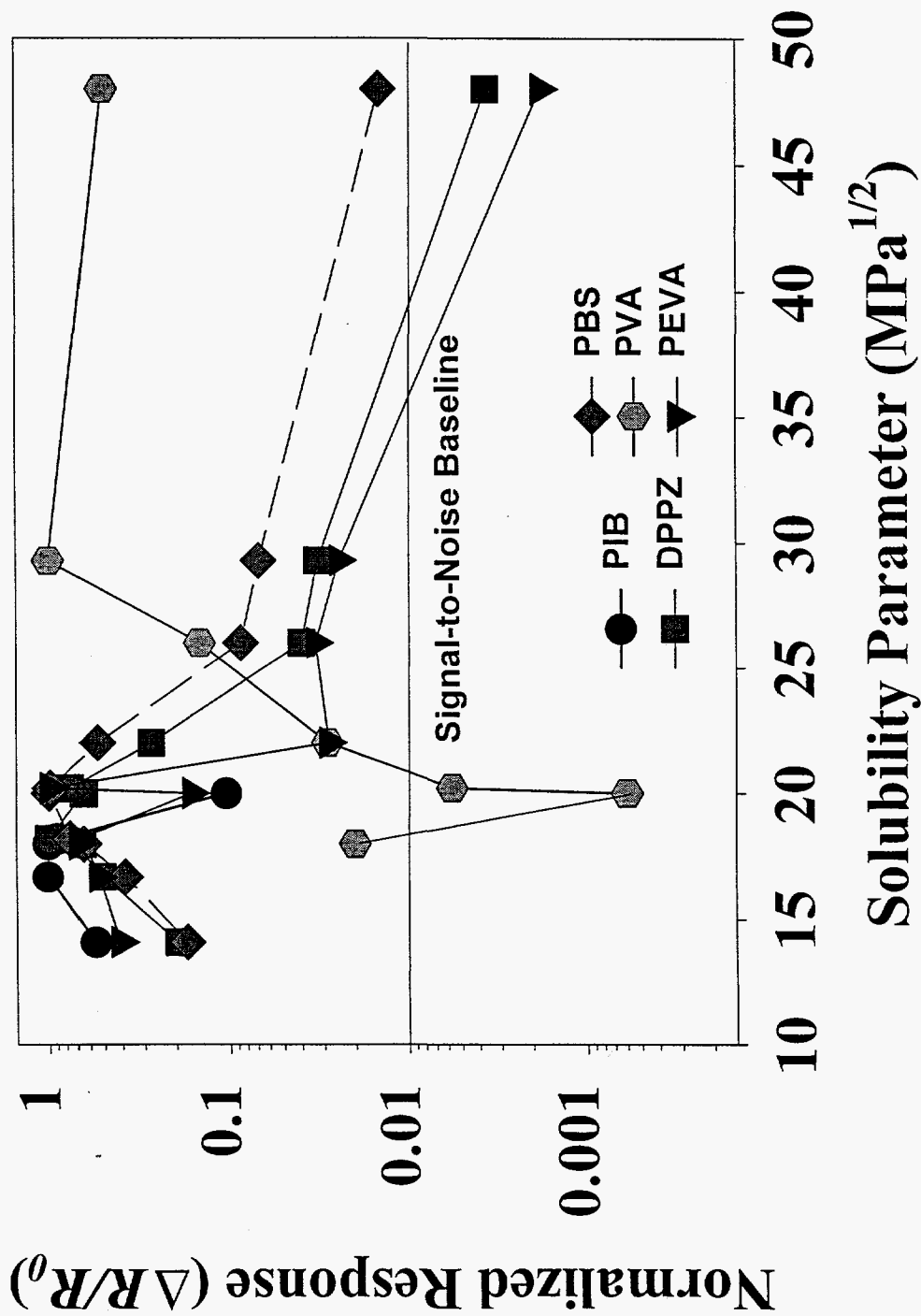


Figure 6/Eastman, et al.

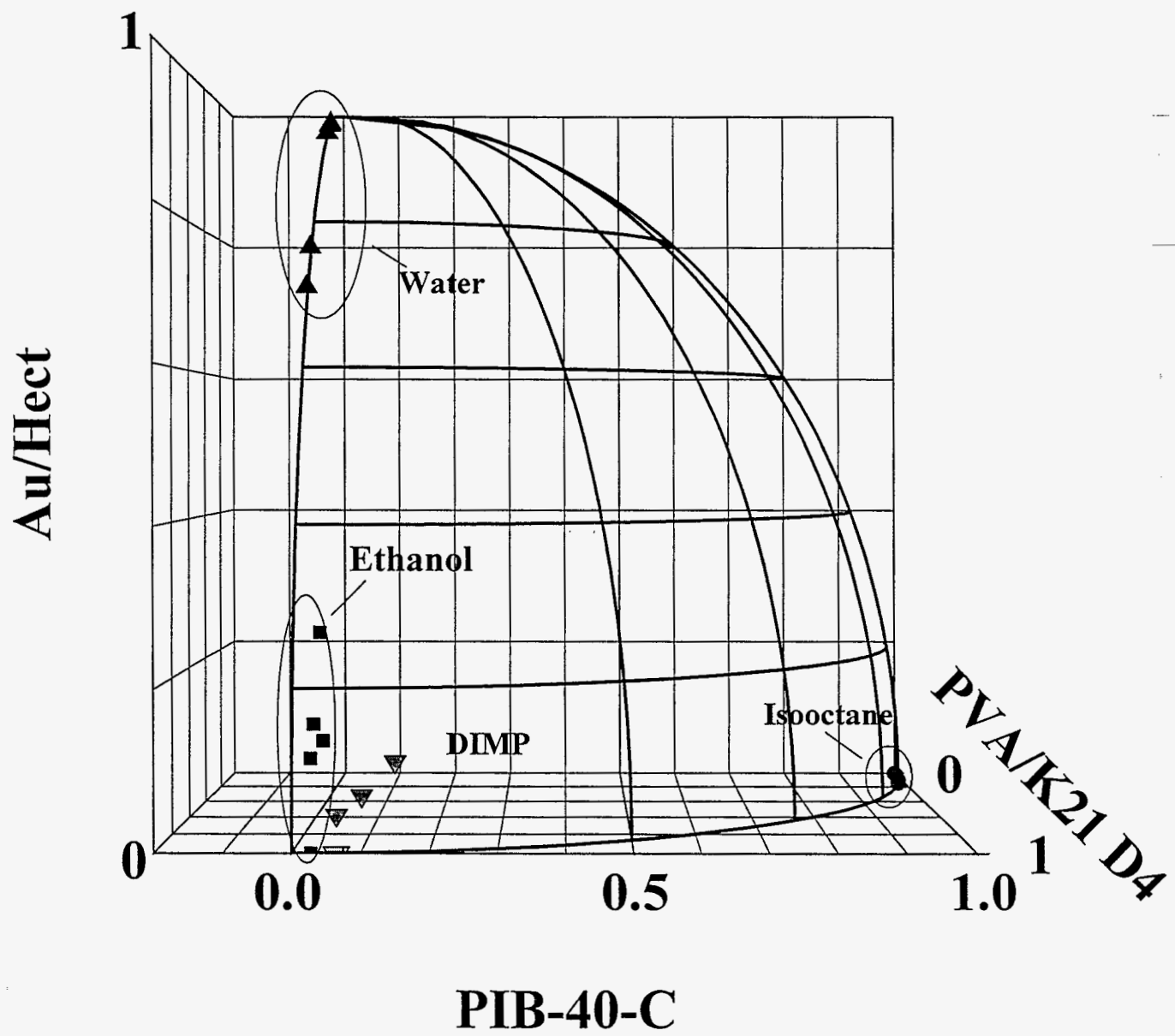


Figure 7/Eastman, et al.

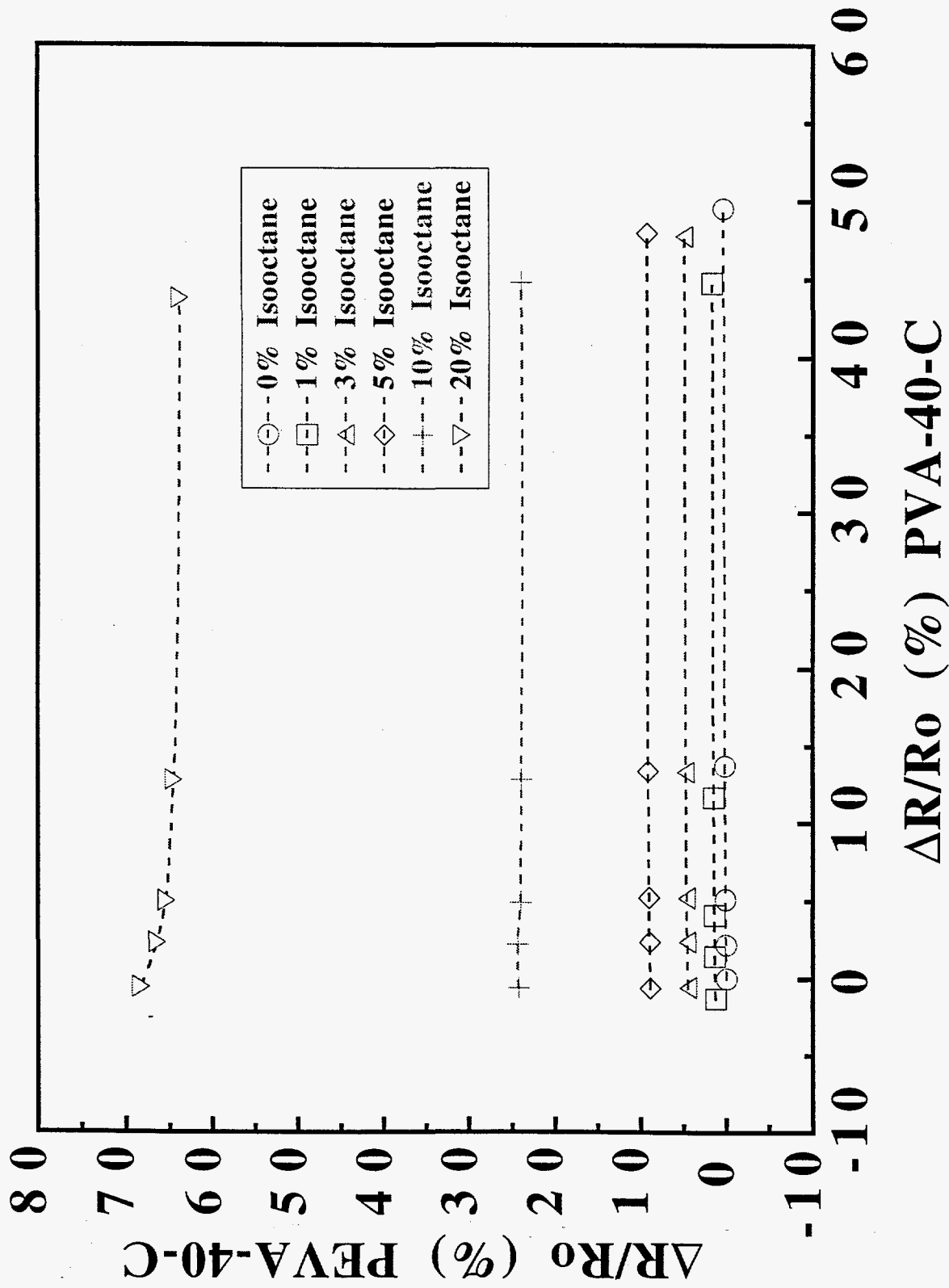


Figure 8/Eastman, et al.

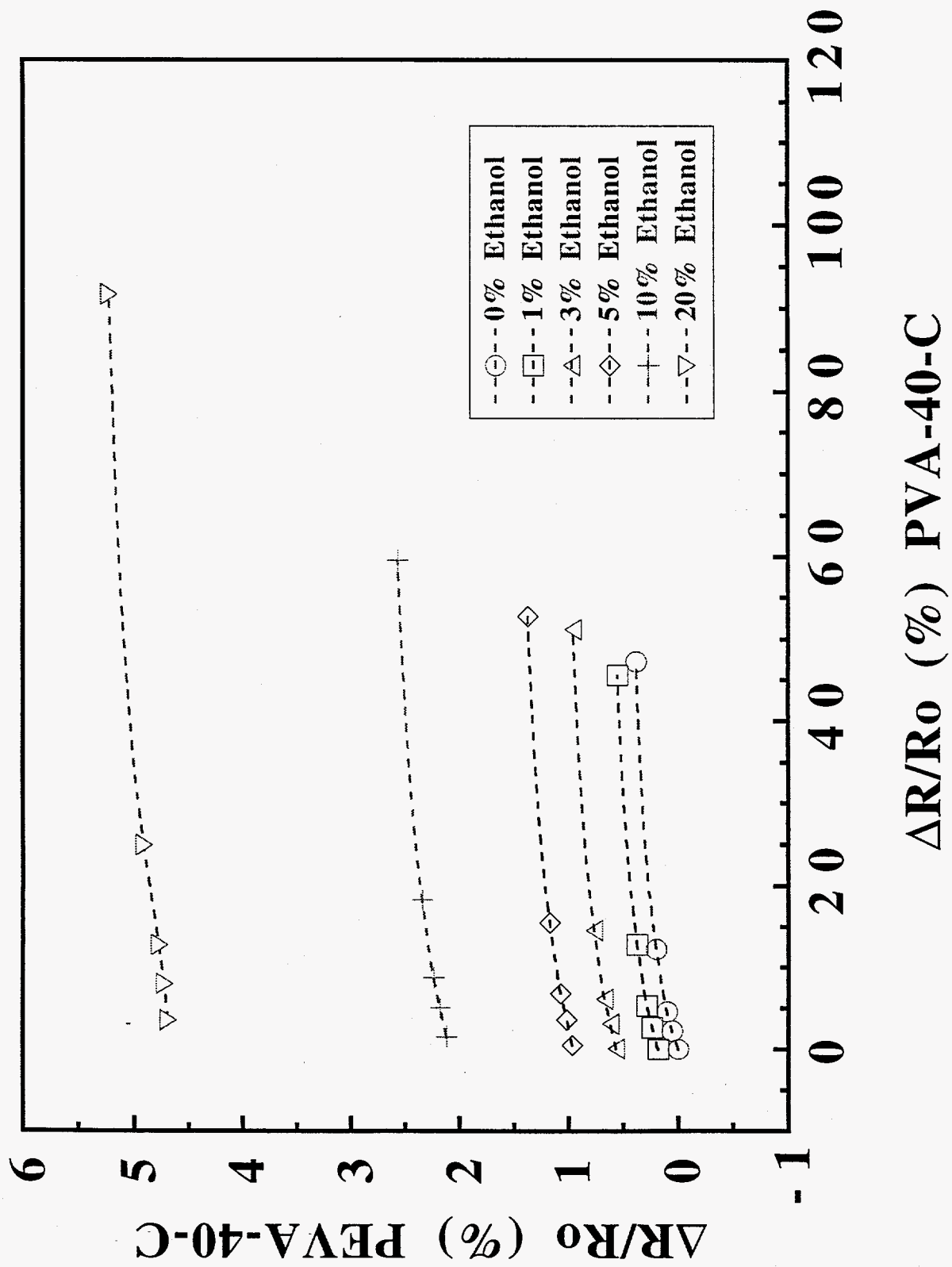


Figure 9/Eastman, et al.

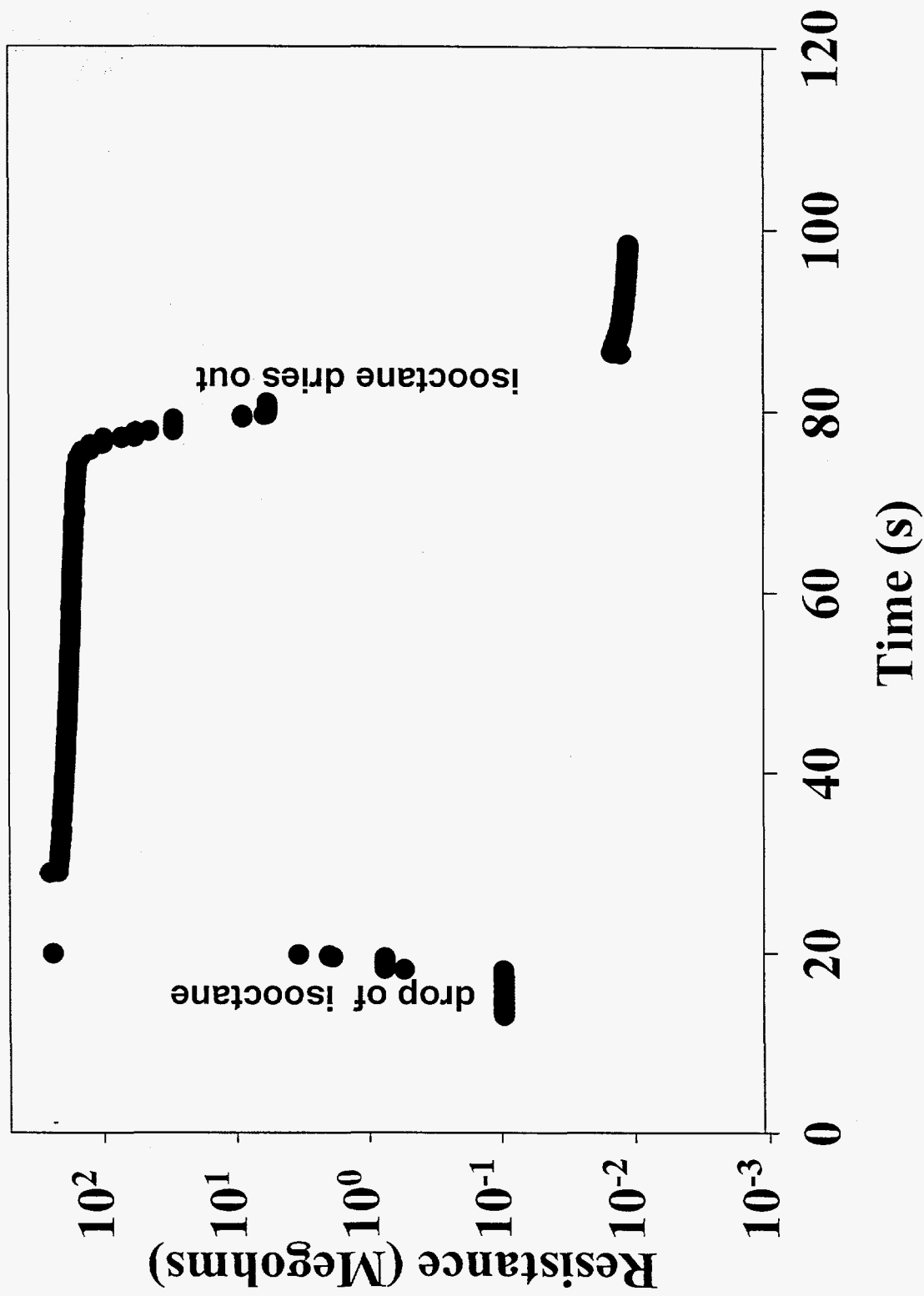


Figure 10/Eastman, et al.