American Chemistry Council | Center for the Polyurethanes Industry

Measuring Residual Catalyst in Polyether Polyols
Guidance by the CPI Polyurethane Raw Materials Analysis Work Group

The CPI Polyurethane Raw Materials Analysis Work Group is familiar with several methods for measuring the amount of residual catalyst in polyether polyols. CPI has supported the development of the following ASTM methods, each of which provides a reliable means for determining residual catalyst in polyether polyols:

- ASTM D4662 - 08(2011)e1 – Standard Test Methods for Polyurethane Raw Materials: Determination of Acid and Alkalinity Numbers of Polyols;
- ASTM D6437 - 05(2010)e1 – Standard Test Method for Polyurethane Raw Materials: alkalinity in Low-Alkalinity Polyols (Determination of CPR values of Polyols); and
- ASTM D7253 - 06(2011)e1 – Standard Test Method for Polyurethane Raw Materials: Determination of Acidity as Acid Number for Polyether Polyols

These ASTM methods provide a reliable and reproducible quantitative result for measuring the catalyst remaining in the polyol (or excess acid used to neutralize the catalyst). These methods contain clear instructions for their use. An added benefit of using these ASTM methods is that the hydroxyl value (as obtained by ASTM D4274) can be corrected using the acidity or alkalinity values determined by the above methods.

Apparent pH as an Indicator of Residual Catalyst

The amount of residual catalyst in the polyol is an important parameter for controlling the formation of polyurethane intermediates. Excess catalyst can lead to gelation or uncontrolled polymerization of products. Polyol producers and customers may use apparent pH measurements as an indicator of residual catalyst in the finished polyol material.

In 1990, a round robin study was performed using three common methods for determining the apparent pH of polyols.[1] The conclusion of the study was that apparent pH measurements are not suitable for determining the amount of acid or base present in polyols due to the high reproducibility of these methods (+/- 0.9 pH units).

Apparent pH measurements typically require the polyol to be dissolved in a mixture of organic solvents and/or water. The pH is then analyzed in the solution. This method may present challenges for the user because the measured pH value does not have the same meaning when measured in organic solvents versus water alone because hydrogen ion activity differs in the two media. A pH of 7 is taken to mean “neutral” in aqueous systems. However, the “neutral point” in organic solvents can be above or below 7 depending on the nature of the solvents, dilution factors, electrode response, and solvent impurities. Polyols may also be given a pH specification without adequately specifying the method (i.e., solvents, dilution) to which the specification applies. This lack of clarity has produced confusion for both suppliers and customers when using apparent pH measurements. The use of the ASTM methods above may help eliminate such confusion and produce more reliable results.

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[1] *Apparent pH of Polyether Polyols - A Comparison of Methods*, from the proceedings of the Society of the Plastics Industry’s 33rd Annual Technical Conference, Polyurethanes 90.

Apparent pH of Polyether Polyols—A Comparison of Methods

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ABSTRACT

Contamination of polyols with trace levels of acid or base can alter product performance greatly. Polyols having an apparent pH greater than 10 may be too reactive with isocyanates causing premature gelling while those with a pH less than 4 may be very slow to react. The determination and interpretation of pH in aqueous media is relatively simple; however, polyols have limited water solubility and require cosolvents. Isopropanol (IPA) and methanol (MeOH) are most commonly used, but the deviation from aqueous conditions introduces uncertainities in the pH determination. Neutrality ($a_{H^+} = a_{OH^-}$) may not correspond to a pH of 7.0, and the pH scale may be different from 0–14. There are also problems with solvent impurities, electrode calibration, and electrode response.

In order to evaluate the pH methods currently in use, the Polyurethanes Raw Materials Analysis Committee (PURMAC) of the Society of the Plastics Industry's Polyurethane Division undertook an intercompany round robin study. Two polyols, Poly-G® 55–56 and VORANOL® 3010, were sent to 12 industrial laboratories representing the major manufacturers of urethane raw materials. Each laboratory was asked to determine pH by three methods: their in-house or internal method, a standard IPA-water method, and a research method designed to exclude carbon dioxide. The nested experimental design and statistical methods described in ASTM Practice E-180 were used to evaluate the data. Duplicability, repeatability, and reproducibility were measured. The standard IPA-water and research methods gave the best results with an interlaboratory reproducibility of 0.3 pH units (1 standard deviation). The pooled internal methods (IPA-water and MeOH-water) showed poor interlaboratory reproducibility with a standard deviation of 0.9 pH units. The MeOH-water methods gave apparent pH values ~1.4 units higher than the IPA-water methods. The statistically different means are attributed to different IPA-water and MeOH-water pH scales.

INTRODUCTION

Apparent pH measurements are commonly used as indicators of acidity and basicity in polyols [1]. pH is defined as the log of the inverse of the hydrogen ion activity: pH = $-\log a_{H^+}$. Polyols with apparent pH's greater than 10 are basic and tend to be highly reactive. Unexpected reactivity can result in premature gelling, reactor fouling, and production losses. Conversely, polyols with measured pH's less than 4 are acidic and react slowly with isocyanates. These are unsuitable for slabstock, spray foam, and RIM applications. The behavior of polyethers with apparent pH's in a neutral range of 5 to 9 is less predictable. This decrease in prediction reliability suggests there may be serious limitations and biases in the commonly used test methods for pH.

The measurement of pH is simple and straightforward for water-soluble samples; however, polyols have limited water solubility and require an organic cosolvent for a pH determination. The common solvents are isopropanol (IPA) and methanol (MeOH). IPA is mixed 10:6 with water, and methanol is mixed 9:1 or 10:1. While IPA-water appears to have a pH range similar to water, MeOH-water differs in pH at neutrality (~8.3) and in range (~0–16.6). Besides different pH scales, the use of organic solvents is accompanied by problems with uncorrected liquid junction potentials, low conductivity, variable solvent purity, dissolved carbon dioxide, and dehydration of the glass electrode. These uncertainties make it difficult to set a realistic pH specification for a neutral polyether.

In order to evaluate the limitations and biases of apparent pH methods, the SPI Polyurethanes Raw Materials Analysis Committee (PURMAC) initiated an intercom-

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pany study comparing the most commonly used methods. Two polyols, Poly G® 55–56 [2] and VORANOL® 3010 [2], were sent to 12 industrial laboratories representing the major manufacturers of urethane raw materials. Each laboratory was asked to determine pH by three methods: the laboratory's in-house method, a standard IPA-water method, and a research method designed to exclude carbon dioxide. All internal methods were either IPA-water or MeOH-water. The protocol followed a nested experimental design and the results were evaluated by the statistical methods described in ASTM Practice E-180 [3].

EXPERIMENTAL PROCEDURES

All laboratories were asked to adhere to a standard IPA-water procedure and a research IPA-water procedure. The MeOH-water determinations followed in-house procedures.

Example of a MeOH-Water Method

APPARATUS

Laboratory pH meter
Combination pH electrode, Corning #476051 or equivalent
Magnetic stirrer
Ordinary laboratory glassware

REAGENTS

Methanol, ACS reagent grade
Methanol-water, 10:1 by weight—e.g., add 100 g of distilled water to 1000 g of MeOH
NaOH solution, ~0.01N—dissolve 0.4 g of sodium hydroxide in 1 liter of distilled water
HCl solution, ~0.01N—dilute 0.8 mL of reagent grade concentrated hydrochloric acid to one liter with distilled water
Standard pH buffer solutions, pH 4.0 and pH 7.0

PROCEDURE

1. Standardize the pH meter using the pH 4.0 and 7.0 buffers, according to the instructions provided with the pH meter.
2. Place 60.0 mL of the water-methanol solution in a 100-mL glass beaker. Using the pH meter as an indicator, neutralize the solvent to pH 7.0 at 25°C with 0.01N HCl or 0.01N NaOH as required. Turn the pH meter to standby, remove the electrode from the solvent.
3. Add 10.0 ± 0.1 g of sample to the neutralized solvent. Mix until complete solution is obtained, using the magnetic stirrer.
4. Immerse the electrode again and determine the pH of the solution at 25°C. Allow an appropriate time for the pH reading to stabilize prior to making the reading.

Standard IPA-Water Method

REAGENTS

Isopropanol-water (10/6 v/v)—mix 10 parts of IPA (ACS Reagent grade, fresh bottle) and 6 parts of distilled water
Hydrochloric acid, ~0.001N, aqueous
Sodium hydroxide, ~0.001N, aqueous
Buffer solutions, pH 7.0 and 4.0

APPARATUS

Expanded scale pH meter or equivalent
Glass electrode, Corning #476022 or equivalent
Calomel electrode, sleeve-type, Corning #476162 or equivalent
Beaker, 100-mL graduated
Magnetic stirrer with stirring bar
Autodispenser, 50-mL

PROCEDURE

1. Calibrate the pH meter with pH 4.0 and 7.0 buffers using the procedure recommended by the instrument manufacturer.
2. Dispense 50 mL of IPA-water into a 100-mL beaker.
3. Immerse the tips of the electrodes into the solvent to a depth not to exceed one-quarter inch above the sleeve of the reference electrode.
4. Add a stirring bar and stir at ~200 rpm.
5. Adjust the pH of the solvent to 7.00 ± 0.01 with dilute sodium hydroxide or dilute hydrochloric acid added dropwise. Only adjust one way. Do not back adjust.
6. Remove electrodes and weigh 10.0 ± 0.1 g sample into the neutralized solvent.
7. Stir until the sample is dissolved.
8. Immerse the tips of the electrodes into the solution as in step 3. Adjust stirring as in step 4.
9. Allow meter to stabilize. This may take several minutes.
10. Read the pH to the nearest 0.01 pH unit.

Research IPA-Water Method

This method is the same as the standard IPA-water method above with one major difference. A sparge tube is placed in the solvent and dry nitrogen is slowly bubbled through the IPA-water to remove carbon dioxide. Purging is stopped for the pH measurements while maintaining the beaker and contents under a nitrogen blanket.

STATISTICAL EVALUATION

The data from the intercompany round robin were evaluated according to ASTM standard recommended practice E180-78, "Developing Precision Data on ASTM Methods for Analysis and Testing of Industrial Chemicals" [3]. The nested or hierarchical design used in the study is shown in Figure 1. Each sample was analyzed in duplicate in each laboratory by a single analyst on each of two different days. All twelve laboratories ran the standard IPA-water method and eleven also ran the research method. Six laboratories ran an internal method in addition to the two methods provided with the distributed protocol. Four of the internal methods used MeOH-water as the solvent, and these data were treated separately from the other data collected by internal methods. The two samples selected

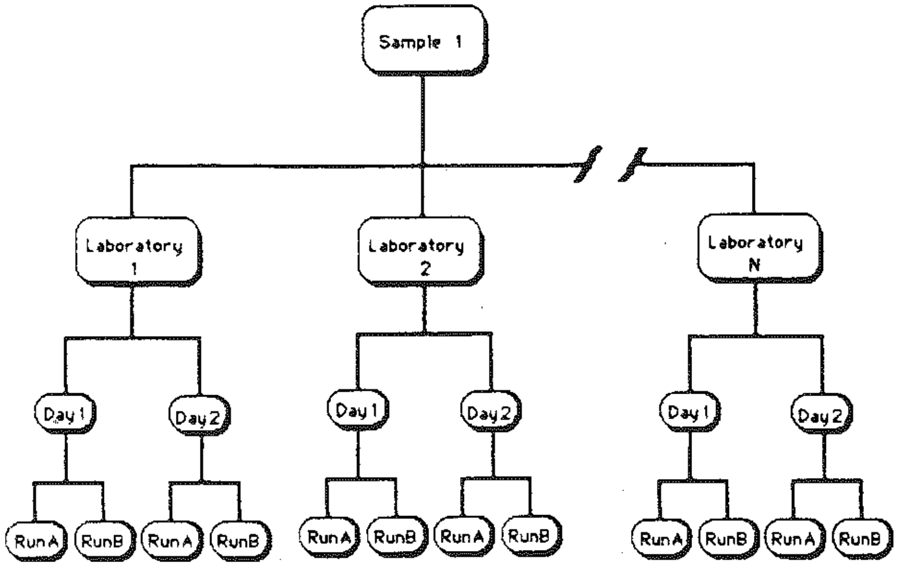

Figure 1. Nested or hierarchical experimental design used.

for the study are commercial polyethers with neutral pH's. They differ in molecular weight, functionality, ethylene oxide content, and hydrophilicity. The data collected are summarized in Tables 1, 2 and 3. Outlying laboratories are marked with an asterisk (*). Data from these laboratories were not used in the calculation of the means or standard deviations.

Statistical Parameters Measured

The standard deviations (S), coefficients of variation (CV), 95% confidence intervals (CI), and the degrees of freedom (DF) for the analyses of both samples were generated according to ASTM Practice E-180 and are compiled in Tables 4, 5, and 6. The variances were shown by the F-test to not be statistically different between samples when run by the same method, so the variances for the two samples for each method were pooled, and the results are shown in the last line of Tables 4, 5, and 6. The pH data generated by internal IPA and MeOH methods were also pooled and analyzed as a single data set, Table 7.

Test for Acceptability of Results

The pooled 95% confidence intervals were used to develop tests for whether a measurement should be accepted or rerun.

- Duplicability (single analyst, same day). Duplicate measurements should be considered suspect (outside the 95% confidence level) if they differ by more than 2% relative, 1.4% relative, and 5.3% relative with the IPA-water method, the research method, and MeOH-water method, respectively.
- Repeatability (single analyst, between days). Two averages of duplicates should be considered suspect (outside the 95% confidence level) if they differ by more than 2.4% relative, 4.9% relative, and 11.2% relative with the IPA-water, research, and MeOH-water methods, respectively.
- Reproducibility (between laboratories). Two averages of duplicates obtained by analysts in different laboratories should be considered suspect (outside the 95% confidence level) if they differ by more than 14.1% relative, 12.5% relative, and 26% relative with the IPA-water, research, and MeOH-water methods, respectively.

Comparison of Results from the Three Methods

Inspection of the means given in Tables 4, 5, and 6 indicates that the MeOH-water method gives pH values ~1.4 units higher than the IPA-water methods. The higher bias of the MeOH-water method was statistically verified by application of the Student's *t*-test (95% confidence level). The means obtained with the two IPA-water methods were also statistically different at the 95% confidence level although the means differ by only ~0.2 units.

Discussion

On the basis of the interlaboratory round robin and on work done in one coauthor's laboratory (RAP), it appears that the goal of quantitatively relating pH to polyol acidity/basicity is presently unattainable. The major problem is the limited solubility of polyols in water. The addition of non-aqueous cosolvents such as alcohols greatly increases the uncertainties in interpreting pH values. Quantitative interpretation of pH also implies very dilute solutions [4] whereas sensitivity considerations require high concentrations of polyether.

Unknown Junction Potentials

A pH test measures a voltage generated between a reference electrode and a measuring electrode (such as a glass pH electrode) that is proportional to the negative log of the hydrogen ion concentration. In addition to the electrode

Table 1. pH data by standard IPA-water method.

Sample	Laboratory Number	Day 1		Day 2		Overall Mean
		Run A	Run B	Run A	Run B	
Poly G® 55-56	1	7.28	7.19	7.20	7.17	6.88
	2	7.13	7.23	7.23	7.25	
	3	6.86	6.88	6.86	6.85	
	4	6.27	6.28	6.26	6.32	
	5	6.63	6.77	6.60	6.51	
	6*	6.97	6.98	6.46	6.79	
	7	6.67	6.67	6.84	6.65	
	8	6.55	6.43	6.29	6.38	
	9	6.68	6.76	6.67	6.66	
	10	6.73	6.72	6.70	6.71	
	11	7.54	7.53	7.43	7.45	
	12	7.48	7.61	7.63	7.65	
VORANOL® 3010	1	7.33	7.25	7.27	7.31	7.14
	2	7.16	7.11	7.16	7.13	
	3	7.11	7.11	7.12	7.11	
	4	7.11	7.06	7.08	7.09	
	5	7.09	7.22	7.12	7.04	
	6	7.13	7.03	6.97	6.98	
	7	7.13	7.03	7.20	7.19	
	8	7.17	7.11	7.07	7.11	
	9	7.25	7.22	7.21	7.25	
	10	7.09	7.11	6.98	6.98	
	11*	7.62	7.57	7.32	7.40	
	12	7.18	7.11	7.18	7.34	

* Outlying laboratories. Data from these laboratories were not used to calculate the means or standard deviations.

Table 2. pH data by research method.

Sample	Laboratory Number	Day 1		Day 2		Overall Mean
		Run A	Run B	Run A	Run B	
Poly G® 55-56	1*	6.58	6.61	6.98	7.16	6.58
	2	6.63	6.64	6.38	6.30	
	3	6.14	6.10	6.13	6.20	
	4	6.43	6.49	6.36	6.40	
	5	7.08	7.08	6.62	6.55	
	6	6.85	6.83	6.93	6.84	
	7	6.50	6.55	6.41	6.37	
	8	6.58	6.60	6.56	6.63	
	9	6.36	6.35	6.32	6.30	
	10	7.25	7.25	7.21	7.22	
	11	6.36	6.33	6.68	6.55	
VORANOL® 3010	1*	7.18	6.93	6.98	7.14	7.08
	2	7.06	7.04	6.95	6.97	
	3	6.87	6.84	6.85	6.84	
	4	7.09	7.07	7.06	7.07	
	5	7.13	7.10	7.12	7.10	
	6	7.06	7.13	7.02	7.05	
	7	7.21	7.19	7.07	7.18	
	8	7.23	7.22	7.24	7.26	
	9	6.95	6.95	6.92	6.93	
	10	7.35	7.35	7.29	7.30	
	11*	7.13	7.16	7.25	7.33	

* Outlying laboratories. Data from these laboratories were not used to calculate the means or standard deviations.

Table 3. pH data by in-house methanol-water methods.

Sample	Laboratory Number	Day 1		Day 2		Overall Mean
		Run A	Run B	Run A	Run B	
Poly G® 55-56	1	8.42	8.48	8.37	8.44	8.35
	2	8.24	8.29	9.21	8.68	
	3	8.62	8.78	8.85	8.85	
	4	7.75	7.34	7.57	7.74	
VORANOL® 3010	1	8.86	8.84	8.77	8.82	8.30
	2	8.04	7.85	8.62	8.74	
	3	7.95	8.30	8.32	8.29	
	4	7.90	7.87	7.84	7.75	

Table 4. Summary of statistical data for standard IPA-water method.

Sample	Mean	Between Runs				Between Days				Between Labs				Number Outliers Excluded
		DF	S	CV	CI	DF	S	CV	CI	DF	S	CV	CI	
Poly G® 55-56	6.89	22	0.055	0.80	2.35	11	0.060	0.87	2.7	10	0.43	6.2	19.6	1
VORANOL® 3010	7.14	22	0.047	0.66	1.92	11	0.052	0.73	2.3	10	0.087	1.2	3.8	1
Pooled	7.02	44	0.051	0.73	2.09	22	0.056	0.80	2.4	10	0.31	4.5	14.1	2

Table 5. Summary of statistical data for research method.

Sample	Mean	Between Runs				Between Days				Between Labs				Number Outliers Excluded
		DF	S	CV	CI	DF	S	CV	CI	DF	S	CV	CI	
Poly G® 55-56	6.58	20	0.038	0.59	1.73	10	0.15	2.24	7.1	9	0.33	5.0	16.0	1
VORANOL® 3010	7.08	18	0.025	0.35	1.05	9	0.035	0.49	1.6	8	0.15	2.1	6.8	2
Pooled	6.83	38	0.033	0.49	1.40	19	0.11	1.66	4.9	9	0.26	3.9	12.5	3

Table 6. Summary of statistical data for methanol-water methods.

Sample	Mean	Between Runs				Between Days				Between Labs				Number Outliers Excluded
		DF	S	CV	CI	DF	S	CV	CI	DF	S	CV	CI	
Poly G® 55-56	8.35	8	0.18	2.15	6.98	4	0.25	2.99	11.54	3	0.55	6.59	28.5	0
VORANOL® 3010	8.30	8	0.11	1.30	4.22	4	0.27	3.26	12.56	3	0.45	5.40	23.4	0
Pooled	8.33	16	0.15	1.77	5.31	8	0.26	3.13	11.70	3	0.50	6.02	26.1	0

Table 7. Summary of statistical data for internal methods (IPA and MeOH).

Sample	Mean	Between Runs				Between Days				Between Labs				Number Outliers Excluded
		DF	S	CV	CI	DF	S	CV	CI	DF	S	CV	CI	
Poly G® 55-56	7.60	10	0.11	1.45	4.55	5	0.066	0.87	3.2	4	1.00	13.2	51.0	1
VORANOL® 3010	7.75	8	0.028	0.36	1.19	4	0.045	0.58	2.2	3	0.78	10.1	43.8	2
Pooled	7.68	18	0.084	1.10	3.28	9	0.058	0.76	2.4	3	0.92	12.0	46.2	3

glass–solution interface, a liquid conductive pathway between the reference electrode and solution being measured also generates a voltage. Although liquid junction potentials exist when pH measurements are taken in aqueous solution, these potentials are effectively canceled out by calibrating the electrode system and determining sample pH's in the same solvent (water). In the case of polyols, pH's are *measured in alcohol-water* while the electrode is *calibrated with aqueous buffer*. Different liquid junction potentials are generated which can equate to several pH units. Also, liquid junction potentials for a given electrode are not constant and are affected by age and changing geometry which can make it impossible to obtain identical pH values at different points in time [5]. Physically, these liquid junctions are small, porous, liquid-filled pathways such as packed asbestos fibers, ceramic frits or ground glass sleeves that constantly bleed reference electrode fluid (typically aqueous KCl) into the measuring solution. Partial pluggage causes resistance changes which give different calibration and measurement responses.

One way to minimize the problem of unknown liquid junction potentials is to use a calibration buffer with the same solvent composition as that used for pH measurements. Unfortunately, few nonaqueous buffer-solvent systems are defined and none are sold commercially. One buffer is the succinate buffer (0.01 molal succinic acid-lithium succinate) which is defined as having a pH of 6.73 in 90% (w/w) MeOH-water [4]. Use of this buffer for electrode calibration gives apparent pH values that are approximately 1 pH unit higher than calibration with aqueous pH 7 buffer. Figure 2 shows a plot of pH vs acid and base added to a neutral polyol as measured in a MeOH water system. The lower curve shows the pH values observed with aqueous calibration of a glass electrode. The other curve gives pH values using lithium succinate/succinic acid calibration in 90% MeOH-water system and is theoretically more accurate. Note the steepness of both curves in the area of neutrality; pH measurements in this region will be particularly susceptible to error.

Non-Aqueous pH Scales

One of the complexities introduced by using non-aqueous solvents for pH measurements is the need for changes in the range of the pH scale. The familiar 0–14 pH range in water is a result of the ionization constant for water, 1×10^{-14} (pK_w 14). Neutrality is when $[H^+] = [OH^-]$ which corresponds to 1×10^{-7} molar concentration or pH 7.

$$H_2O \rightarrow H^+ + OH^-$$

$$K_w = \frac{[H^+]\,[OH^-]}{[H_2O]} = 1 \times 10^{-14}$$

$$-\log K_w = pK_w = 14$$

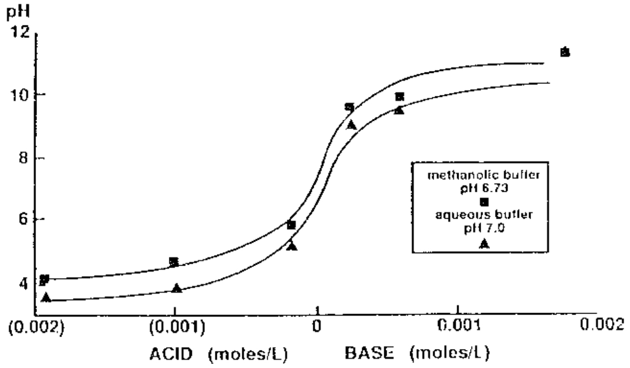

Figure 2. Effect of different electrode calibration methods on apparent pH of 2000 MW polypropylene glycol. Dilute KOH or HCl (0.001 M) was added to adjust basicity or acidity.

Use of solvents other than water produces other ionization constants and, therefore, other pH ranges. For instance, the ionization constants for pure MeOH and IPA are 16.7 and 20.8, respectively [6]. The corresponding neutral points are 8.3 and 10.4. Unfortunately, the ionization constants are not available for aqueous mixtures of these alcohols. In addition, when polyol pH is measured in these two solvent mixtures, the polyol contributes to the ionization constant. This is because large concentrations of polyol are used in the standard pH methods (10–15%) and different alcohols (polyols) have different ionization constants. Primary alcohols are more acidic than secondary [7], and different polyols have different primary/secondary hydroxyl ratios.

The above discussion indicates that it is not possible to exactly calculate the neutral point in these non-aqueous systems. However, it is very probable that in a 90% MeOH solvent the ionization constant is near that of the MeOH, and the neutral point would be about 8.1 if the ionization constants are proportional to concentration. In aqueous IPA (38% water), the ionization constant would be nearer that of water and indeed the apparent pH values of polyols found in the round robin are near 8.3 in MeOH-water and 7 in IPA-water.

Solvent Purity

With the low levels of acidity or basicity seen in these polyols, even trace amounts of acidic or basic substances can have significant effects on measured pH. For this reason one has to be very concerned with the solvents being used. Preferably, water should be deionized and MeOH (or IPA) should be of reagent grade. Different grades, different suppliers, and even different bottles of MeOH from the same supplier can act differently in titrations and pH measurements. No precise studies have been made of this effect, but it has been reported [8] that MeOH and IPA can be contaminated with trace amounts of trimethylamine (ostensibly from the catalytic production process).

If trimethylamine is present at the 1×10^{-4} moles/L level, this can overshadow the effect of acid/base in the polyol. Assuming an apparent pH variation of 0.5 pH units, this calculates to an acid (or base) concentration of only 3×10^{-8} moles/L using MeOH with an assumed pK of 16. To correct for trace amounts of acid or base in the measuring solvent, the standard pH procedures adjust the starting pH to a "neutral" pH 7 by addition of dilute solutions of strong acid or base. If the solvent already contains a weak base (or acid such as carbon dioxide), this step can generate small amounts of buffering agent (salt of weak acid-strong base or vice versa) which will affect the pH measurement.

There are two other very important problems with the pH adjustment of the starting solvent. One is consistency. Some samples require large adjustments, others not at all or somewhere in-between. Another factor is that pH 7 is not the neutral point when pH is measured with methanolic solvent. The addition of acid or base to a starting pH of 7 produces a slightly acidic solvent. Not only is accuracy gone, but reproducibility is also affected. One way to avoid or minimize this problem is to pre-treat the alcohol by passing it through a short column of mixed acid/base ion exchange resin to remove traces of such impurities.

Dissolved CO_2

Carbon dioxide is an acidic gas by virtue of its reaction with water to form the weak carbonic acid with a pK_a = 6.37. Since the solvent system used for pH may or may not be saturated with CO_2, this constitutes another variable. While the pH measurements under nitrogen did not increase in value in the round robin, a closely controlled experiment did show the expected variation between standard off-the-shelf solvent and one that was thoroughly sparged with nitrogen, Figure 3. As expected, the solvent system free of CO_2 showed slightly higher pH values in the region of basic polyol.

Conductivity

A somewhat unexpected factor affecting pH measurement of polyols is a problem associated with low conductivity. Although pH measurements are best done in dilute solution, too low a level of acid/base or other conducting ions can also cause problems. This is often seen even in aqueous systems when trying to do pH measurements of very pure water such as boiler feed. There appears to be a strong relationship of liquid junction potential with ionic strength (conductivity) of the solution. If some solvent samples require more (or less) adjustment with acid or base they may also produce variable liquid junction potentials which can vary as much as 20 mv (0.3 pH units) [9].

Glass Electrode Storage

A final variable that can be expected to contribute to pH measurement variability is storage of the glass combination electrode. Since pH measurements of polyols are done in non-aqueous solvents, one has to be concerned about the method of storage between measurements. In all aqueous measurements, this is not very important and the electrode can even be allowed to dry out between uses [7]. However, for intermittent use in non-aqueous solvents the situation can be quite different.

For example, should the electrode be stored in water (ionic or deionized) or the alcoholic solution? If stored in alcohol, will the glass membrane dehydrate and require hydration time before measurement? Will the reference junction plug more quickly because of KCl precipitation? Conversely, if stored in water will there be an acclimation period which varies with subsequent samples? All of these factors can play a role in the variability of measured values. To preserve reproducibility, electrode storage should at least be standardized.

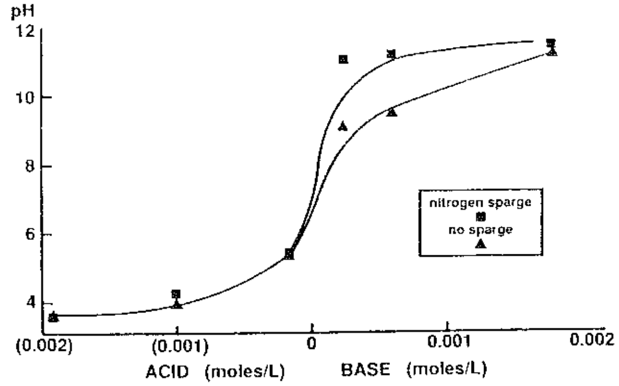

Figure 3. Effect of carbon dioxide on apparent pH of 2000 MW polypropylene glycol. Carbon dioxide was removed by sparging with nitrogen.

CONCLUSIONS

This round robin study indicates a reproducibility (between labs, internal methods) of ±0.9 pH units for "neutral" samples, Table 7. The high standard deviation is attributed to the steep slope of the pH curve in the 5–9 region and uncontrollable variations in solvent pK's, solvent purity, and electrode behavior. If a single method is agreed upon and used, the reproducibility is better (S = 0.3–0.5), Tables 4–6.

Apparent pH measurements are not suitable for determining the amount of acid or base present in polyols. Quantitative calculations require exact knowledge of the neutral point of the alcohol/water/polyol system. The common perception that pH 7 represents neutrality is *not* true when using high alcohol levels in the measuring solvent. An apparent pH measurement in 10/6 IPA-water of 7.7 indicates basicity while the same value in 90/10 MeOH-water indicates acidity. A much better method to measure polyol acidity or basicity is by titration. Use of appropriate sample sizes, solvents and titration reagents can produce excellent results.

Apparent pH measurements may be used qualitatively, i.e., as an indicator of consistency in production or contamination in shipping. However, manufacturing and customer specifications should take into account the intra- and interlaboratory standard errors of measurements as determined by this or similar round robin study.

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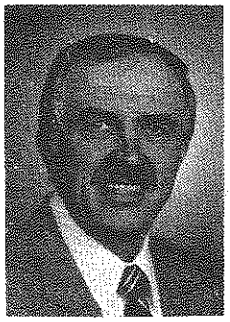

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