

INTERNATIONAL UNION OF PURE  
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION  
COMMISSION ON ELECTROANALYTICAL CHEMISTRY

**pH MEASUREMENTS IN NON-AQUEOUS AND MIXED  
SOLVENTS: PREDICTING pH(PS) OF POTASSIUM  
HYDROGEN PHTHALATE FOR ALCOHOL–WATER  
MIXTURES**

(Technical Report)

*Prepared for publication by*

S. RONDININI, P. R. MUSSINI, T. MUSSINI AND A. VERTOVA

Department of Physical Chemistry and Electrochemistry,  
University of Milan, Via Golgi 19, 20133 Milano, Italy

*Membership of Commission V.5:* *Chairman:* R. A. Durst (USA; 1989–91); R. P. Buck (USA; 1991–99); *Secretary:* K. M. Kadish (USA; 1989–91); K. Tóth (Hungary; 1991–95), S. Rondinini Cavallari (Italy; 1995–97); W. Kutner (Poland; 1997–99). *Titular Members:* M. F. Camoes (Portugal; 1995–99); M. Gross (France; 1987–91); W. Kutner (Poland; 1995–97), M. L'Her (France; 1991–95); E. Lindner (Hungary; 1997–99), S. Rondinini Cavallari (Italy; 1991–95 and 1997–99); K. Štulík (Czech Republic; 1989–97); K. Tóth (Hungary; 1987–91); Y. Umezawa (Japan; 1991–99); *Associate Members:* A. M. Bond (Australia; 1989–97); K. Cammann (Germany; 1989–95); M. F. Camoes (Portugal; 1989–95); A. G. Fogg (UK; 1987–97); L. Gorton, (Sweden; 1994–99); W. R. Heineman (USA; 1991–95); S. Kihara (Japan; 1991–99); W. F. Koch (USA; 1991–95), W. Kutner (Poland; 1989–95); E. Lindner (Hungary; 1995–97); R. Naumann (Germany; 1995–99); K. W. Pratt (USA; 1995–99); Prabhakara Rao (India; 1989–93); S. Rondinini Cavallari (Italy; 1987–91); K. Štulík (Czech Republic; 1987–91 and 1997–99); Y. Umezawa (Japan; 1987–91); H. P. van Leeuwen (the Netherlands; 1985–1993); E. Wang (China; 1987–1995); J. Wang (USA; 1991–1999). *National Representatives:* S. S. M. Hassan (Arab Republic of Egypt; 1994–1999); J.-M. Kauffmann (Belgium; 1991–99); I. R. Gutz (Brazil; 1994–99); H. B. Kristensen (Denmark; 1988–99); T. Mussini (Italy; 1989–99); H. P. van Leeuwen (Netherlands; 1994–99); H. Kim (Republic of Korea; 1994–99); D. R. Groot (Republic of South Africa; 1994–99); Y. Vlasov (Russia; 1995–99); D. Bustin (Slovakia; 1994–99); A. Covington (1987–99); F. Kadirgan (Turkey; 1994–99); B. Pihlar (Slovenia; 1994–99). Names of countries given after Members' names are in accordance with the *IUPAC Handbook 1994–95* (Blackwell).

---

*Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference to the source along with use of the copyright symbol ©, the name IUPAC and the year of publication are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.*

# pH measurements in non-aqueous and mixed solvents: Predicting pH(PS) of potassium hydrogen phthalate for alcohol-water mixtures (Technical Report)

*Abstract:* Predictive equations for estimating pH(PS) (PS = Primary Standard) of the potassium hydrogen phthalate buffer in any aqueous-alcoholic mixture are given as functions of the alcoholic moiety mole fraction,  $x$ , in the mixture and of the relative permittivity,  $\epsilon$ , and the autoprotolysis constant,  $pK_{ap}$ , of the pure alcohol at 298.15 K. The two equations, one valid for 298.15 K and the other covering the 263 – 318 K temperature range, have been optimized by using the experimental data of pH(PS) in aqueous mixtures with the following alcohols: methanol, ethanol, propan-2-ol, ethane-1,2-diol, 2-methoxyethanol (“methylcellosolve”). The equations, tested on subsets generated from the full-set by removing an entire co-solvent at a time, provide predicted pH(PS) values which differ from the “true” ones by less than 0.1 pH over the entire range of co-solvent composition:  $0 < x \leq 0.75$ . The predictive equations are recommended for calculating pH(PS) only in those aqueous-alcoholic media for which the corresponding experimental values are not available, and not as smoothing equations for water and its mixtures with the above-mentioned solvents.

## INTRODUCTION

Recently, recommended pH(PS) (PS = Primary Standard) values of potassium hydrogen phthalate 0.05 m buffer solution in aqueous-organic solvent mixtures have been reported (ref. 1) for the following organic co-solvent in the mixtures: methanol (ref. 2), ethanol (ref. 1,3), propan-2-ol (ref. 2,4), ethane-1,2-diol (ref. 1,5), 2-methoxyethanol (ref. 1,6), acetonitrile (ref. 7), 1,4-dioxane (ref. 8) and dimethyl sulfoxide (ref. 9).

Although the above-mentioned set of recommended values covers some of the most often used aqueous-organic solvent mixtures, it is evident that the set is far from being complete. Hence, urgent need emerges of providing reliable estimates of the pH(PS) values, especially for those solvent mixtures for which direct experimental determinations have not yet been performed.

Therefore, it is proposed here that, in absence of directly determined values in mixed solvents, the pH(PS) be calculated by using a predictive equation that relates the sought values to selected, easily accessible properties of the relevant pure organic co-solvents at 298.15 K.

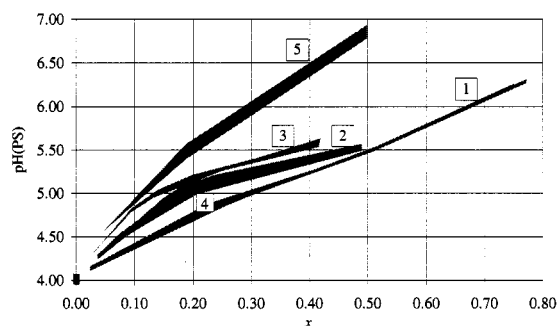
## RESULTS

Among the 8 co-solvents studied so far (ref. 1), alcohols constitute a wide, homogeneous and highly significant set, since they include differently functionalised molecules with quite different physico-chemical properties. For the sake of clarity, the pH(PS) domains for the five families of alcohol–water mixtures are represented in Fig. 1 as a function of the alcohol mole fraction,  $x$ . For each family, the shaded area marks the variations of pH(PS) within the appropriate temperature range.

The predictive equation is restricted to alcohol-water mixtures. Out of many physico-chemical properties, relative permittivity ( $\epsilon$ ) (ref. 10-13), autoprotolysis constant ( $pK_{ap}$ ) (ref. 14 Note A ) of the pure alcohol component at 298.15 K, temperature and alcohol mole fraction ( $x$ ) of the mixture, have been chosen as the most significant variables by a multiregression analysis procedure.

---

Note A : for the autoprotolysis constant of 2-methoxyethanol, in the absence of specific literature value, that of 2-ethoxyethanol ( $pK_{ap} = 19.3$ ) has been taken as the best approximation



**Fig. 1** Primary Standards of potassium hydrogen phthalate for various alcohol–water mixtures, in the  $263 \leq T \leq 318$  K range, as a function of the mole fraction,  $x$ , of the alcoholic moiety. Shaded areas show the domains of the alcoholic component: 1 = methanol; 2 = ethanol; 3 = propan-2-ol; 4 = ethane-1,2-diol; 5 = 2-methoxyethanol

The following predictive equation, valid at  $T = 298.15$  K:

$$\text{pH(PS)} = 4.005 + 21.62x - 8.6x^{3/2} + 31.5x^2 - 0.807\epsilon x + 0.01029\epsilon^2 x - 1.56K_{\text{ap}}x^2 \quad (1)$$

was obtained by forcing the intercept (given in italics) to coincide with the pH(PS) in water at 298 K. Equation (1) has root mean square error = 0.035, and then provides pH(PS) values which differ from the recommended values in reference (ref. 1) always by less than 0.1 pH, over the whole range of solvent compositions.

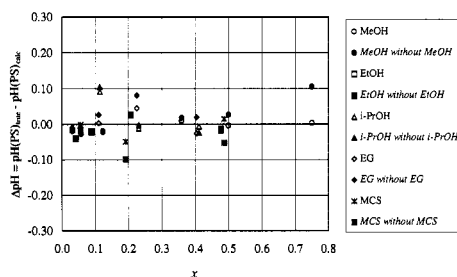
Equation (1) was verified as follows: one co-solvent at a time was removed from the set of data, regression coefficients were reoptimised, and the differences,  $\Delta\text{pH}$ , between calculated and true pH(PS)'s were redetermined. Special attention was paid to the predicted differences referring to each omitted solvent in turn, since these will be a good measure of the reliability of estimated data: again few 0.01 pH were obtained on average, the most discordant result being the  $\approx 0.1$   $\Delta\text{pH}$  for ethanol of mol fraction  $\approx 0.2$  (mass fraction 0.4).

By extending the prediction to the 263 – 318 K temperature range, one obtains a 7 term version of the equation:

$$\text{pH(PS)} = 4.005 + 22.17x - 9.19x^{3/2} + 32.26x^2 - 0.821\epsilon x + 0.01049\epsilon^2 x - 1.590K_{\text{ap}}x^2 - 0.75u_1x^{1/2} \quad (2)$$

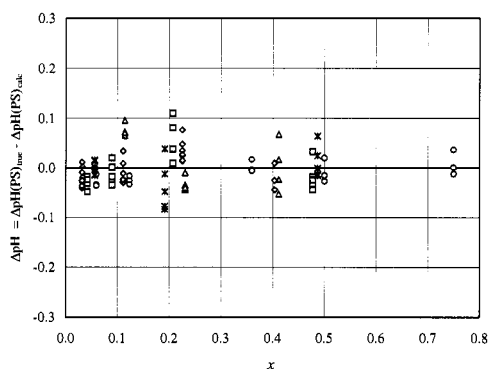
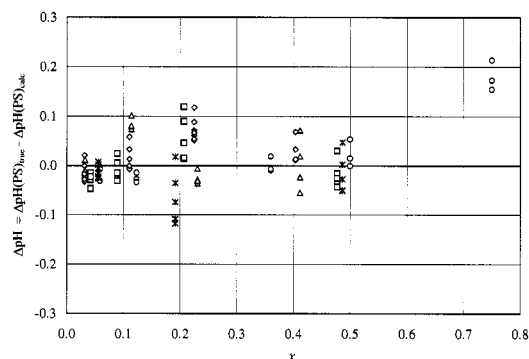
(where  $u_1 = z/(1+z)$ ,  $z = (T-\theta)/\theta$  and  $\theta = 298.15$  K), which provides estimated values of the same accuracy as that indicated above. In fact, the highest deviations are 0.15 – 0.2  $\Delta\text{pH}$  for methanol of mol fraction  $\approx 0.75$  (mass fraction 0.842), when methanol is omitted.

Figures 2–4 summarise the results. The  $\Delta\text{pH}$  values are plotted against alcohol mole fraction,  $x$ , for both "none-omitted" and "one-omitted" cases at  $T = 298.15$  K in Fig. 2, the "all  $T$  - none omitted" case in Fig. 3, and the "all  $T$  - one omitted" case in Fig. 4.



**Fig. 2**  $\Delta\text{pH}$  from equation (1),  $T = 298$  K (Note B)

Note B The abbreviations for the last three solvents have been derived from their trivial names, isopropyl alcohol, ethylene glycol, and methylcellulosolve, respectively

Fig. 3  $\Delta\text{pH}$ : "all  $T$  – none omitted" (Note B)Fig. 4  $\Delta\text{pH}$ : "all  $T$  – one omitted" (Note B)

## CONCLUSIONS

The presented equations are recommended for reliable estimations of the  $\text{pH}(\text{PS})$  values in aqueous–alcoholic mixtures in absence of the experimental determinations. Predictive equation (2) is valid in the  $263 \leq T \leq 313 \text{ K}$  range and for co-solvent molar fraction up to 0.75 (provided that the permittivity of the mixture exceeds 35), while predictive equation (1) covers the same composition range, at  $T = 298.15 \text{ K}$ .

## REFERENCES

- 1 P.R.Mussini, T.Mussini, and S.Rondinini, *Pure Appl. Chem.* **69**, 1007 (1997)
- 2 T. Mussini, A. K. Covington, F. Dal Pozzo, P. Longhi, S. Rondinini, and Zi-Ya Zou, *Electrochim. Acta* **28**, 1593 (1983)
- 3 P. Longhi, P. R. Mussini, T. Mussini, and S. Rondinini, *J. Chem. Eng. Data* **34**, 64 (1989)
- 4 S. Rondinini, P. Longhi, P. R. Mussini, A. Nese, M. Pozzi, and G. Tiella, *Anal. Chim. Acta* **207**, 211 (1988)
- 5 T. Mussini, P. Longhi, I. Marcolungo, P. R. Mussini, and S. Rondinini, *Fresenius's Zeit. Analyt. Chemie* **339**, 608 (1991)
- 6 F. Arrigoni, P. R. Mussini, T. Mussini, and S. Rondinini, *J. Solut. Chem.* **24**, 1267 (1995)
- 7 S. Rondinini, and A. Nese, *Electrochim. Acta* **32**, 1499 (1987)
- 8 T. Mussini, A. K. Covington, M. Cicognini, P. Longhi, and S. Rondinini, *Anal. Chim. Acta* **162**, 103 (1984)
- 9 M.J.Taylor, *J. Chem. Eng. Data* **24**, 230 (1979).
- 10 Y. Marcus, and S. Glikberg, *Pure Appl. Chem.* **57**, 855 (1985)
- 11 Y. Marcus, *Pure Appl. Chem.* **57**, 860 (1985)
- 12 Y. Marcus, *Pure Appl. Chem.* **58**, 1411 (1986)
- 13 Y. Marcus, *Pure Appl. Chem.* **62**, 139 (1990)
- 14 S. Rondinini, P. Longhi, P.R. Mussini, and T. Mussini, *Pure Appl. Chem.*, **59**, 1693 (1987)