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Reference Value Standards for pH Measurements, and First Ionization Constants of *o*-Phthalic Acid, in Ethanol/Water Solvent Mixtures at Temperatures from −5 to +40 °C

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Reference value standards, pH_{RVS}, for 0.05 mol kg^{-1} potassium hydrogenphthalate (KHPh) reference buffer solutions in 10, 20, 40, and 70 wt % ethanol/water solvent mixtures from −5 to +40 °C have been determined from reversible emf measurements of the cell $Pt|H_2|KHPh + KCl|AgCl|Ag|Pt$. The large set of such emf values (546 cells) has been analyzed in terms of a multilinear regression method recommended in recent IUPAC documents. Ancillary values of the first ionization constant of *o*-phthalic acid (H_2Ph; benzene-1,2-dicarboxylic acid, the parent acid to KHPh), required for the above calculations, have been determined from reversible emf measurements of the cell $Pt|H_2|H_2Ph + KHPh + KCl|AgCl|Ag|Pt$ (421 data), over the same range of solvent compositions and temperatures.

Introduction

Rules and procedures for pH standardization in water, organic solvents, and water + organic solvent mixtures have been defined by recent IUPAC documents (*1*, *2*) which for each such solvent recognize the pH of the 0.05 *m* potassium hydrogenphthalate (KHPh) buffer solution as the reference value standard (RVS). The several other popular standard buffers (phosphate, acetate, carbonate, citrate, succinate, etc.) are assigned a subordinate role with respect to the above RVS buffer (*1*, *2*), and for the determination of their respective pH values in solvents other than pure water (*1*) or heavy water (*3*, *4*), it is evident that electrochemists have hitherto concentrated their efforts almost exclusively on ethanol, methanol, and their mixtures with water (*3*). The situation is better for the RVS buffer, whose pH_{RVS} values are now known for water (*1*), heavy water (*3*, *4*), and binary aqueous mixtures with a greater variety of organic solvents: i.e., methanol (*3*, *5*), dimethyl sulfoxide (*3*, *6*), 1,4-dioxane (*3*, *7*), acetonitrile (*3*, *8*, *9*), ethanol (*3*), and 2-propanol (*3*). In spite of the importance of ethanol as a solvent (both at normal and subzero temperatures) in the bio-physio-medical domain, a first and overdue determination of pH_{RVS} in ethanol/water mixtures (*3*), together with pH_{RVS} for 2-propanol/water mixtures (*3*), became available the latest.

The aim of the present work is the critical reassessment of pH_{RVS} values for 0.05 *m* KHPh over the −5 to +40 °C temperature range, based on the IUPAC-approved scheme (*3*) of multilinear regression analysis of a *large* set of appropriate emf data (546 cells) for ethanol/water mixture up to 70 wt % ethanol, which is the upper limit for the absence of ionic association in such mixed solvents.

To this purpose, systematic measurements have been made of the reversible emf E_1 of cell 1:

$$Pt|H_2(1\ atm)|KHPh(m_{RVS}) + KCl(m_{Cl})|AgCl|Ag|Pt \qquad (1)$$

within the temperature range from 268.15 to 313.15 K, at fixed molality m_{RVS} = 0.05 mol kg^{-1} for KHPh but at various molalities m_{Cl} of KCl (0.005–0.100 mol kg^{-1}) in ethanol/water mixtures at 10, 20, 40, and 70 wt % ethanol. In fact, the key Nernstian function of E_1 for the evaluation of pH is

$$(E_1 - E°)/k = p(a_H a_{Cl}) = pH + pm_{Cl} + p\gamma_{Cl} \qquad (2)$$

where $k = (\ln 10)RT/F$, p = −log, pH is the current symbol for pa_H, and subscript ionic species are indicated without charge numbers to simplify printing. Equation 2 requires knowledge of the relevant values of the standard emf $E°$ of cell 1; these have been redetermined recently (*3*, *10*).

In addition, systematic measurements of the reversible emf E_3 of cell 3

$$Pt|H_2(1\ atm)|H_2Ph(m_1) + KHPh(m_2) + KCl(m_3)|AgCl|Ag|Pt \qquad (3)$$

have been carried out at various molalities of the mixed electrolyte ($0.005 < m_1 < 0.050$ mol kg^{-1}), within the same ranges of temperature and solvent composition explored with cell 1, to determine accurate values of the relevant first ionization constant, K_I, of *o*-phthalic acid (H_2Ph; benzene-1,2-dicarboxylic acid), which are essential to the present scheme of data processing.

Experimental Section

The silver/silver chloride electrodes in cells 1 and 3 were prepared according to the electrolytic method (*11*). The hydrogen electrodes were of the same type already used for the previous pH_{RVS} determinations in methanol/water (*5*), acetonitrile/water (*8*, *9*), and 1,4-dioxane/water (*7*) solvent mixtures. An average of about four independent cells were measured at each electrolyte molality and at each temperature, for a total of 546 emf's in the case of cell 1 and 421 emf's in the case of cell 3. The potentiometric and the thermostatic apparatus were described earlier (*12*). Each measured emf value was corrected to 1 atm (101 325 Pa) pressure of hydrogen from the barometic pressure and the vapor pressure of the solution, the latter being taken as the same as the vapor pressure of the solvent (*13*–*16*). The solutions were made up by weight from redistilled deionized water, analytical grade Baker ethanol, *o*-phthalic acid and potassium chloride, and certified ULTREX Baker potassium hydrogenphthalate; before use, the last three chemicals were dried at 110 °C (*1*). Values of relative permittivities (dielectric constants), ϵ, and densities, ρ, of the solvents involved in the calculation of the Debye–Hückel constants A and a_0B in eq 5 and 6 have been taken from data in the literature (*15*, *17*–*19*).

Results and Discussion

***Reference Value Standards for pH Measurements*, pH_{RVS}.** From eq 2 it is clear that the quantity

$$p(a_H\gamma_{Cl}) = pH + p\gamma_{Cl} = (E_1 - E°)/k - pm_{Cl} \qquad (4)$$

can be determined in thermodynamically exact terms, but to obtain pH therefrom for the mixed electrolyte in cell 1, it is indispensable to calculate the single Cl^- ion term $p\gamma_{Cl}$ through an extrathermodynamic assumption, i.e., a form of the classical Debye–Hückel equation

$$p\gamma_{Cl} = AI^{1/2}/(1 + a_0BI^{1/2}) \qquad (5)$$

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Table I. The emf E_1 of Cell 1 at Various Molalities m_{Cl} of KCl in 0.05 m Potassium Hydrogenphthalate for Various Ethanol/Water Solvent Mixtures at Different Temperatures T

$10^3 m_{Cl}$, mol kg^{-1}	E_1, mV at T, K					$10^3 m_{Cl}$, mol kg^{-1}	E_1, mV at T, K				
	268.15	273.15	283.15	298.15	313.15		268.15	273.15	283.15	298.15	313.15
10 wt % Ethanol											
5.005	582.15	587.27	595.70	607.49	619.26	29.996	540.14	543.64	550.58	560.45	569.40
5.005	582.15	587.96	595.51	607.76	619.47	29.996	540.02	543.30	550.34	559.99	569.27
5.005		587.47	595.73		619.48	29.996	540.16	543.37	550.45	560.02	569.35
5.005		587.22	595.61		619.69	29.996				560.36	
5.005		587.53			618.47	29.996				560.54	
5.005		587.57				49.987	527.87	531.25	537.63	546.42	555.25
10.011	566.00	569.97	577.80	588.82	599.87	49.987	527.97	531.37	537.81	546.42	555.40
10.011	565.75	569.64	577.53	588.81	599.61	49.987	527.77	531.13	537.52	546.33	555.22
10.011		569.99	577.77	589.09	599.83	49.987	527.88	531.33	537.62	546.48	555.34
10.011		569.74	577.47	588.82	599.54	70.003	519.32	522.42	528.45	537.02	545.55
20.010	549.60	553.48	561.03	570.12	580.06	70.003	519.14	522.22	528.19	536.98	545.24
20.010	549.90	553.72	561.03	570.36	580.28	70.003	519.22	522.30	528.40	537.36	545.64
20.010	549.46	553.30	561.06	570.88	580.08	70.003	519.08	522.17	528.07	537.29	545.48
20.010	549.83	553.60	561.07	571.68	580.38	99.999	510.95	513.93	519.56	527.37	534.82
20.010				570.72		99.999	511.09	514.09	519.76	527.38	534.94
20.010				571.42		99.999	510.79	513.87	519.54	527.65	534.81
29.996	540.03	543.51	550.42	560.51	569.34	99.999	510.91	514.03	519.72	527.77	534.91
20 wt % Ethanol											
5.017	590.01	594.52	603.38	616.38	628.96	30.006	546.82	550.67	558.42	569.29	579.90
5.017	590.17	594.66	603.45	616.38	628.74	30.006	546.84	550.39	558.07	569.51	579.17
5.017	590.05	594.45	603.39	616.22	628.98	30.006					579.92
5.017	590.01	594.57	603.39	616.06	628.75	30.006					579.24
10.029	573.80	578.46	586.89	598.57	609.00	50.015	534.84	538.44	545.78	555.26	563.86
10.029	574.24	578.51	586.92	598.63	608.95	50.015	535.24	538.66	545.78	555.19	563.97
10.029	574.11	578.17	586.82	598.48	609.00	50.015	535.12	538.56	545.53	555.34	564.14
10.029	574.13	578.52	586.89	598.60	608.82	50.015	535.08	538.74	545.73	555.62	564.18
10.029				598.65		69.986	525.58	529.02	536.45	545.96	554.71
10.029				598.83		69.986	525.50	528.96	536.50	546.07	554.51
20.027	557.10	561.08	568.88	580.79	590.82	69.986	525.58	529.05	535.88	546.55	554.68
20.027	557.14	561.36	569.16	580.79	590.72	69.986	525.42	528.96	536.19	546.56	554.54
20.027	557.10	561.06	568.82	580.29	590.73	100.017	517.31	520.59	527.21	535.89	544.24
20.027	556.76	561.34	569.16	580.48	590.56	100.017	517.81	521.29	527.64	536.23	544.22
30.006	546.92	550.73	558.53	569.50	578.46	100.017	517.29	520.64	527.49	536.53	544.24
30.006	546.83	550.41	558.46	569.46	578.38	100.017	517.75	521.30	527.48	536.55	544.28
40 wt % Ethanol											
5.036	612.94	616.60	623.00	633.38	642.66	29.989	570.47	572.84	577.89	585.27	592.62
5.036	612.67	616.30	623.16	633.42	642.57	29.989	570.35	572.97	578.35	585.21	592.58
5.036	613.12	616.53	623.13	632.99	642.68	49.975			564.02	570.63	577.69
5.036	612.92	616.35	623.19	633.12	642.49	49.975			564.02	570.60	577.48
10.029	596.35	599.25	606.23	614.23	623.09	49.975				570.74	577.93
10.029	596.24	599.41	606.64	614.28	623.23	49.975				570.77	577.79
10.029	596.48	599.24	605.44	614.21	623.12	70.026	548.69	550.83	554.59	561.19	566.83
10.029	596.42	599.48	605.57	614.36	623.43	70.026	548.52	550.81	554.94	561.18	566.79
20.045	580.44	583.01	588.78	594.85	604.03	70.026	548.51	550.74			
20.045	580.84	583.38	589.07	595.06	603.98	70.026	548.56	550.79			
20.045	581.02	583.07	588.84	596.99	605.23	100.035	539.10	541.16	545.23	550.87	556.50
20.045	580.99	583.48	589.16	597.18	605.33	100.035	538.99	541.17	545.22	550.98	556.50
29.989	570.08	572.97	577.74	585.04	592.47	100.035	539.21	541.03	545.19	551.07	
29.989	570.53	573.34	578.04	585.00	592.42	100.035	539.18	540.97	545.19	551.14	
70 wt % Ethanol											
4.994	617.35	619.40	623.58	631.31	638.32	15.022	590.94	592.98	596.84	602.51	608.31
4.994	617.22	619.10	623.46	631.08	638.01	19.990	584.21	585.00	588.09	593.57	598.81
4.994	617.63	619.57	623.70	631.48	638.28	19.990	584.18	585.21	588.21	593.61	598.99
4.994	617.43	619.50	623.77	631.30	638.20	19.990	584.16	585.15	588.23	594.07	599.15
4.994					638.31	19.990	584.14	585.40	588.38	594.12	599.33
4.994					628.25	24.978	578.20	579.68	582.75	587.65	593.00
10.021	600.82	603.00	605.93	611.69	618.82	24.978	578.32	579.83	582.93	587.93	593.22
10.021	600.45	602.65	605.78	611.39	618.58	24.978	578.07	579.75	582.89	587.96	593.06
10.021	600.36	602.87		611.41	618.88	24.978	578.56	579.84	583.05	588.21	593.29
10.021	600.34	602.55			618.62	30.029	573.79	575.10	577.76	582.34	586.89
10.021		601.80				30.029	573.39	574.75	577.65	582.24	586.78
10.021		601.75				30.029	573.75	575.17			587.12
10.021		602.15				30.029	573.32	574.74			586.94
10.021		602.09				39.985	566.45	567.70	570.18	574.32	578.80
15.022	590.84	592.92	596.59	602.21	607.98	39.985	566.34	567.64	570.19	574.61	579.08
15.022	590.53	592.99	596.61	602.36	608.15	39.985	566.31	567.85	570.27	574.46	578.89
15.022	591.04	592.98	596.77	602.31	608.12	39.985	566.31	567.84	570.28	574.75	579.12

where A and B are the Debye–Hückel constants and a_0 is the ion-size parameter in the solvent mixture considered. The relevant E_1 values are collected in Table I, and the required values of the standard emf E° have been redetermined recently (*3*, *10*). In compliance with IUPAC rules (*2*, *3*), the value of the a_0B product in eq 5 is assigned at the appropriate tem-

Table II. Standard $\mathrm{pH_{RVS}}$ Values of 0.05 *m* Potassium Hydrogenphthalate Buffers (with Relevant Standard Errors), at Various Temperatures and Various Compositions (Weight Percentages of Ethanol, with Corresponding Mole Fractions *x*) of Ethanol/Water Mixtures, as Obtained from One-Stage Multilinear Regression Analysis of the All-*T* All-*x* E_1 Data Set Altogether on the Basis of Eq 12

temp		$\mathrm{pH_{RVS}}$ values			
K	°C	10 wt % EtOH (x = 0.041 64)	20 wt % EtOH (x = 0.089 05)	40 wt % EtOH (x = 0.206 79)	70 wt % EtOH (x = 0.477 11)
268.15	−5	4.276 ± 0.001	4.564 ± 0.001	5.113 ± 0.001	5.525 ± 0.002
273.15	0	4.258 ± 0.001	4.542 ± 0.001	5.079 ± 0.001	5.504 ± 0.001
283.15	10	4.235 ± 0.001	4.514 ± 0.001	5.027 ± 0.001	5.478 ± 0.001
298.15	25	4.234 ± 0.001	4.504 ± 0.001	4.985 ± 0.001	5.471 ± 0.001
313.15	40	4.264 ± 0.001	4.526 ± 0.001	4.979 ± 0.002	5.497 ± 0.002

Table III. Coefficients d_i of the Multilinear Regression Eq 12 for $\mathrm{pH_{RVS}}$ (cf. Tables I and II), with Relevant Standard Errors, Covering the Various Ethanol/Water Solvent Mixtures from 0 to 70 wt % Ethanol over the Temperature Range from 268.15 to 313.15 K

d_0	3.9947 ± 0.0008	d_6	−3.44 ± 0.13
d_1	−0.404 ± 0.024	d_7	0.3604 ± 0.0098
d_2	8.33 ± 0.12	d_8	−32.99 ± 0.67
d_3	−15.18 ± 0.44	d_9	67.8 ± 1.4
d_4	11.38 ± 0.56	d_{10}	13.22 ± 0.26
d_5	−0.809 ± 0.020		

Table IV. Values of Standard emf $E°$[a] (of Cells 1 and 3), Debye-Hückel Parameters A[b] and a_0B,[c] Densities ρ,[d] and Relative Permittivities (Dielectric Constants) ϵ_ϵ, at Various Temperatures and Weight Percentages of Ethanol in Admixture with Water, Used for Processing E_1 and E_3 Data

wt % EtOH		*T*, K				
		268.15	273.15	283.15	298.15	313.15
10	$E°$	227.12	225.90	222.46	214.94	204.70
	A	0.5764	0.5754	0.5746	0.5721	0.5732
	a_0B	1.574	1.573	1.565	1.548	1.536
	ρ	0.9850	0.9841	0.9839	0.9804	0.9748
	ϵ	80.00	78.64	75.89	72.20	68.52
20	E^0	218.44	217.66	214.88	207.76	197.26
	A	0.6499	0.6486	0.6456	0.6440	0.6451
	a_0B	1.635	1.633	1.621	1.602	1.588
	ρ	0.9790	0.9772	0.9725	0.9664	0.9586
	ϵ	73.70	72.43	69.95	66.40	62.98
40	E^0	212.04	209.58	203.93	193.68	181.41
	A	0.7873	0.7954	0.8080	0.8387	0.8749
	a_0B	1.734	1.737	1.729	1.728	1.734
	ρ	0.9630	0.9590	0.9424	0.9315	0.9199
	ϵ	64.51	62.82	59.57	55.00	50.79
70	$E°$	190.20	185.53	175.41	158.36	139.196
	A	1.2755	1.2951	1.3374	1.4068	1.4859
	a_0B	1.982	1.989	1.996	2.002	2.015
	ρ	0.8880	0.8840	0.8760	0.8634	0.8503
	ϵ	45.51	44.16	41.57	37.98	34.69

[a] In mV. [b,c] In $\mathrm{mol^{-1/2}\ kg^{1/2}}$. [d] In $\mathrm{kg\ dm^{-3}}$.

perature *T* by an extension of the Bates–Guggenheim convention (*1–3*), in terms of

$$[a_0B]_T = [\epsilon^{\mathrm{w}}\rho^{\mathrm{s}}/(\epsilon^{\mathrm{s}}\rho^{\mathrm{w}})]_T^{1/2} \tag{6}$$

where the superscripts w and s refer to pure water and to the appropriate solvent mixture, respectively.

Calculation of $\mathrm{p}\gamma_{\mathrm{Cl}}$ through eq 5 requires knowledge of the ionic strength I of the mixed electrolyte

$$I = I_{\mathrm{RVS}} + m_{\mathrm{Cl}} = m_{\mathrm{Cl}} + (m_{\mathrm{RVS}} + m_{\mathrm{H}} + m_{\mathrm{HPh}} + 4m_{\mathrm{Ph}})/2 \tag{7}$$

where the molality of the hydrogenphthalate ion, m_{HPh}, is given by (*20*)

$$m_{\mathrm{HPh}} = m_{\mathrm{RVS}} + m_{\mathrm{H}} - 2m_{\mathrm{Ph}} \tag{8}$$

and that of the phthalate ion, m_{Ph}, is given by (*9*)

$$m_{\mathrm{Ph}} = m_{\mathrm{H}}(m_{\mathrm{RVS}} + m_{\mathrm{H}} + K_{\mathrm{I}}/(\gamma_{\mathrm{H}}\gamma_{\mathrm{HPh}}))/(2m_{\mathrm{H}} + K_{\mathrm{I}}/(\gamma_{\mathrm{H}}\gamma_{\mathrm{HPh}})) \tag{9}$$

I, m_{HPh}, and m_{Ph} are, in turn, functions of the $\mathrm{H^+}$ molality, m_{H}, as expressed by

$$\mathrm{p}m_{\mathrm{H}} = (E_1 - E°)/k - \mathrm{p}m_{\mathrm{Cl}} - \mathrm{p}(\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}) \tag{10}$$

and of the first ionization constant, K_{I}, of the *o*-phthalic acid ($\mathrm{H_2Ph}$).

Preliminary knowledge of K_{I} and iterative calculations involving eq 5–10 are necessary to obtain I and $\mathrm{p}\gamma_{\mathrm{Cl}}$ for each composition of the KHPh + KCl mixed electrolyte solution, and the further assumption

$$\gamma_{\mathrm{H}} = \gamma_{\mathrm{Cl}} = \gamma_{\mathrm{HPh}} \tag{11}$$

is used throughout. K_{I} data for the present range of solvent composition were hitherto completely lacking; thus their determination had to be carried out in the present work from systematic emf measurements on cell 3 which are described in the next paragraph. Inserting $\mathrm{p}\gamma_{\mathrm{Cl}}$ in eq 4, one distinct pH value is obtained for each molality m_{Cl} examined. The standard value, $\mathrm{pH_{RVS}}$, obviously for KHPh *alone* at the fixed molality $m_{\mathrm{RVS}} = 0.05\ \mathrm{mol\ kg^{-1}}$, can finally be obtained as intercept at $m_{\mathrm{Cl}} = 0$ from the pH vs m_{Cl} linear regression at each mole fraction x of ethanol and at each temperature T. The results are, however, optimized in terms of IUPAC recommendations (*3*) by interpreting the all-T all-x E_1 data set *altogether* through a one-stage multilinear regression scheme (*5*, *7–9*) of the type

$$\mathrm{pH} = d_0 + \sum_{i=1}^{10}(d_iv_i) \tag{12}$$

where the independent variables v_i are functions of m_{Cl}, T, and x in the following terms: $v_1 = x^{1/2}$; $v_2 = x$; $v_3 = x^2$; $v_4 = x^3$; $v_5 = m_{\mathrm{Cl}}$; $v_6 = xm_{\mathrm{Cl}}$; $v_7 = z/(1 + z)$; $v_6 = v_7x^2$; $v_9 = v_7x^3$; $v_{10} = \ln(1 + z) - v_7$; and $z = (T - 298.15)/298.15$. The resulting $\mathrm{pH_{RVS}}$ values are quoted in Table II, together with their respective standard errors. The values of the multilinear regression coefficients d_i of eq 12 (including the intercept d_0) are quoted in Table III: the number of E_1 data processed is 546. The selected values for the quantities $E°$, A, a_0B, ρ, and ϵ required by eq 2–6 are collected in Table IV.

First Ionization Constant of o-Phthalic Acid. Values of the first ionization constant (K_{I}) of *o*-phthalic acid, which are required for the iterative calculations described in the preceding paragraph, were hitherto missing. Therefore, they have been now determined from systematic measurements of the emf E_3 of cell 3 within the temperature range from −5 to +40 °C in 10, 20, 40, and 70 wt % ethanol/water mixtures at different molalities of the mixed electrolyte $\mathrm{H_2Ph}$ + KHPh + KCl. The functional equation for E_3 is

$$(E_3 - E°)/k + \log[m_3(m_1 - m_{\mathrm{H}})/(m_2 + m_{\mathrm{H}})] = \mathrm{p}K_{\mathrm{I}} + (b_{\mathrm{HPh}} - b_{\mathrm{Cl}})I = \psi \tag{13}$$

where b_{HPh} and b_{Cl} are the specific interaction parameters of the extended Debye–Hückel equations for $\mathrm{p}\gamma_{\mathrm{HPh}} = AI^{1/2}/(1 + a_0BI^{1/2}) - b_{\mathrm{HPh}}$ and for $\mathrm{p}\gamma_{\mathrm{Cl}} = AI^{1/2}/(1 + a_0BI^{1/2}) - b_{\mathrm{Cl}}$, respectively, and, of course, the standard emf $E°$ is the same as that for cell I. Neglecting the small contribution of the

Table V. The emf E_3 of Cell 3 at Various Molalities of the Mixed Electrolyte $H_2Ph(m_1)$ + $KHPh(m_2)$ + $KCl(m_3)$ in Different Ethanol/Water Solvent Mixtures at Various Temperatures T

10^3m_1, mol kg^{-1}	E_3, mV, at T, K					10^3m_1, mol kg^{-1}	E_3, mV, at T, K				
	268.15	273.15	283.15	298.15	313.15		268.15	273.15	283.15	298.15	313.15
10 wt % Ethanol^a											
4.884	525.30	528.50	534.65	542.71	550.34	14.630	496.15	499.58	504.74	512.11	517.37
4.884	525.37	528.06	534.61	542.70	550.50	14.630	496.44	499.59	505.07	512.31	517.59
4.884	525.28	529.00	534.76	542.97	550.47	19.520	488.73	491.84	497.30	504.27	509.33
4.884	525.50	529.06	534.77	542.97	550.69	19.520	489.06	491.84	497.24	504.25	508.94
7.316	514.18	518.20	524.25	531.34	538.24	19.520	489.00	491.83	497.08	503.88	509.09
7.316	514.60	517.96	524.52	531.40	538.54	19.520	489.03	491.82	497.04	503.81	508.59
7.316	514.23	517.81	524.10	531.37		19.520				504.22	
7.316	514.58	518.20	524.46	531.68		19.520				504.07	
9.770	506.40	509.73	515.83	523.03	528.97	29.280		482.13	486.98	493.36	497.22
9.770	506.48	509.72	515.85	523.11	529.01	29.280		482.39	487.10	493.41	497.35
9.770	506.39	509.58	515.77	523.38	529.48	29.280			487.06	493.90	497.62
9.770	506.39	509.60	515.77	523.46	529.30	29.280			457.12	493.82	497.58
14.630	496.34	499.62	504.70	512.38	517.55	29.280				493.02	
14.630	496.52	499.66	505.01	512.38	517.54	29.280				493.02	
20 wt % Ethanol^b											
10.000	510.73	513.73	519.07	525.63	530.61	20.000	493.82	496.63	500.81	506.71	511.04
10.000	510.78	513.81	519.07	525.70	530.76	20.000	493.58	496.35	500.97	506.72	510.47
10.000	510.73	513.69	519.14	525.54	530.44	20.000	493.81	496.56	501.11	506.69	511.17
10.000	510.63	513.79	519.19	525.56	530.54	30.400	484.41	486.46	490.57	495.33	498.61
15.000	500.83	503.82	508.35	514.79	519.17	30.400	484.23	486.45	490.68	495.28	498.51
15.000	500.78	503.65	508.25	514.70	519.16	30.400	484.52	486.45	490.61	495.36	498.63
15.000	501.08	503.70	508.43	514.02	519.08	30.400	484.51	486.38	490.72	495.31	498.54
15.000	500.97	503.55	508.41	513.98	519.05	40.000		479.31	484.18	487.62	490.85
15.000					519.02	40.000		479.72	483.70	487.64	490.73
15.000					519.00	40.000		479.24	484.16	487.63	490.92
20.000	493.62	496.49	500.62	506.71	510.19	40.000		479.84	484.01	487.75	490.86
40 wt % Ethanol^b											
10.000	518.60	519.34	521.63	524.91	527.12	30.000	492.98	493.44	494.83	496.63	497.34
10.000	518.62	519.55	522.00	524.88	527.08	30.000	492.77	493.52	494.78	496.79	497.23
10.000		519.24	521.74	524.87	526.65	30.000	493.04	493.37	494.80	496.44	497.44
10.000		519.67	522.06	524.80	527.08	30.000	492.85	493.44	494.86	496.65	497.46
15.000	508.69	509.93	511.88	513.45	516.09	40.000	485.32	485.66	487.63	488.04	489.94
15.000	509.04	510.13	511.99	513.61	516.31	40.000	485.42	485.77	487.73	487.97	489.86
15.000		509.61	511.75	514.06	515.99	40.000		485.99			490.05
15.000		510.11	512.02	514.17	516.22	40.000		485.09			489.65
20.000	502.35	502.12	504.45	506.40	508.19	50.000	481.02	481.87	482.45	483.39	484.53
20.000	502.49	502.11	504.59	506.38	508.23	50.000	481.32	482.04	482.78	483.68	484.37
20.000	502.30	502.44	504.47	506.44	508.16	50.000				483.44	483.96
20.000	502.25	502.43	504.78	506.80	508.08	50.000				483.80	484.17
70 wt % Ethanol^b											
10.000	513.03	513.50	513.66	513.51	513.21	20.000		497.90	497.15	496.16	494.85
10.000	513.34	513.60	513.81	513.83	513.53	30.000	489.09	488.24	487.09	485.57	483.75
10.000	513.20	513.61	513.64	513.85	513.14	30.000	489.46	488.62	487.12	485.70	483.97
10.000	513.49	513.63	513.81	514.17	513.47	30.000	488.82	488.31	487.14	485.52	483.90
15.000	504.04	503.83	503.41	503.28	502.27	30.000	489.16	488.50	487.11	485.74	484.17
15.000	504.23	504.01	503.58	503.40	502.48	40.000	482.72	481.92	480.36	478.63	476.57
15.000	504.06	504.14	503.46	503.32	502.34	40.000	482.81	482.15	480.68	478.78	476.65
15.000	504.24		503.65	503.41	502.59	40.000	483.01	482.14	480.67	478.66	476.56
20.000	498.28	497.25	496.35	495.85	494.41	40.000	482.93	482.36	480.94	478.82	476.61
20.000	497.80	497.85	497.06	495.69	494.87	40.000		482.13	480.85		
20.000		497.42	496.57	496.15	494.47	40.000		482.35	481.04		

[a] $m_1 = 0.996m_2 = 0.976m_3$. [b] $m_1 = m_2 = m_3$.

Table VI. Values of the First Ionization Constant K_I (Given as pK_I) of *o*-Phthalic Acid (with Corresponding Standard Errors) Relevant to Various Percentages of Ethanol in Admixture with Water, at Various Temperatures as Obtained from emf Measurements of Cell 3

temp		pK_I values			
K	°C	10 wt % EtOH	20 wt % EtOH	40 wt % EtOH	70 wt % EtOH
268.15	-5	3.192 ± 0.002	3.446 ± 0.003	3.739 ± 0.004	4.046 ± 0.002
273.15	0	3.169 ± 0.003	3.422 ± 0.002	3.689 ± 0.005	4.027 ± 0.002
283.15	10	3.140 ± 0.004	3.361 ± 0.002	3.627 ± 0.002	3.993 ± 0.002
298.15	25	3.117 ± 0.003	3.324 ± 0.002	3.557 ± 0.003	3.985 ± 0.002
313.15	40	3.143 ± 0.002	3.318 ± 0.002	3.519 ± 0.002	3.997 ± 0.001

second ionization constant (K_{II}) of *o*-phthalic acid, which in water is lower than K_I by about 3 orders of magnitude (*7*), one can write the ionic strength of the cell 3 electrolyte as

$$I = m_2 + m_3 + m_{\mathrm{H}} \tag{14}$$

Determining I again requires an iterative calculation cycle, as described in earlier works (*5*, *7–9*) for each molality of the mixed electrolyte at which E_3 was measured. Finally, plotting ψ vs I produces a straight line, the intercept of which at I = 0 gives a distinct pK_I value for each solvent composition and temperature. Table V collects the E_3 values (the relevant $E°$'s are to be found in Table IV) and Table VI the resulting pK_I values with the corresponding standard errors.

Conclusions

It must be emphasized that each pH_{RVS} value is valid only for the pH scale relevant to the specific (pure or mixed) solvent s considered (2, 7) and would be conveniently identified, e.g., by superscript s as $^{s}pH_{RVS}$. Values of $^{s}pH_{RVS}$ pertaining to different solvents would become physically comparable on an "intersolvental" pH scale with ultimate reference to the familiar pH scale in water (w) only by being preliminarily converted to $^{s}_{w}pH_{RVS}$ values by the equation (*2*)

$$^{s}_{w}pH_{RVS} = {}^{s}pH_{RVs} + ({}^{w}E°_{H} - {}^{s}E°_{H})/k \qquad (15)$$

where $^{w}E°_{H}$ and $^{s}E°_{H}$ would be the absolute standard potentials (i.e., referred to a hypothetical electrode having standard potential invariant with varying solvent composition) of the hydrogen electrode in water and in the solvent mixture, respectively. The difference $^{w}E°_{H} - {}^{s}E°_{H}$ represents the so-called primary medium effect (*21*), is a measure of the Gibbs free energy of transfer of the H^+ ion from water to the solvent mixture, and, as such, is another extrathermodynamic quantity. An approach to its difficult quantification was recently made available (*22*).

Another interesting feature is that $^{s}pH_{RVS}$ is a continuous and smooth function of solvent composition and temperature, and sets of $^{s}pH_{RVS}$ data for an increasing number of aqueous mixtures with a variety of nonaqueous solvents can be processed together in terms of the above multilinear regression method to set up improved equations for *predicting* (*9*, *23*) reliable $^{s}pH_{RVS}$ values in still uninvestigated aqueous-organic solvent mixtures. The present data set provides an useful contribution also in such a context.

Registry No. *o*-Phthalic acid, 88-99-3; KH phthalate, 877-24-7.

Literature Cited

(1) Covington, A. K.; Bates, R. G.; Durst, R. A. *Pure Appl. Chem.* **1965**, *57*, 531. Original works: Hamer, W. J.; Acree, S. F. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1944**, *32*, 215. Hamer, W. J.; Pinching, G. D.; Acree, S. F. *Ibid.* **1946**, *36*, 47. Hetzer, H. B.; Durst, R. A.; Robinson, R. A.; Bates, R. G. *Ibid.* **1977**, *81A*, 21. Bütikofer, H. P.; Covington, A. K. *Anal. Chim. Acta* **1979**, *108*, 179. Bates, R. G.; Acree, S. F. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1945**, *34*, 373. Bates, R. G. *Ibid.* **1947**, *39*, 411. Manov, G. G.; DeLollis, N. J.; Lindvall, P. W.; Acree, S. F. *Ibid.* **1946**, *36*, 543. Bower, V. E.; Bates, R. G. *Ibid.* **1957**, *59*, 261. Bates, R. G.; Bower, V. E.; Miller, R. G.; Smith, E. R. *Ibid.* **1951**, *47*, 433. Staples, B. R.; Bates, R. G. *Ibid.* **1969**, *73A*, 37. Paabo, M.; Bates, R. G. *Anal. Chem.* **1969**, *41*, 283.

(2) Mussini, T.; Covington, A. K.; Longhi, P.; Rondinini, S. *Pure Appl. Chem.* **1965**, *57*, 865.

(3) Rondinini, S.; Mussini, P. R.; Mussini, T. *Pure Appl. Chem.* **1987**, *59*, 1549.

(4) Yung-Chi-Wu; Koch, W. F. *J. Solution Chem.* **1986**, *15*, 481.

(5) Mussini, T.; Covington, A. K.; Dal Pozzo, F.; Longhi, P.; Rondinini, S.; Zi-Ya-Zou *Electrochim. Acta* **1983**, *28*, 1593.

(6) Taylor, M. J. *J. Chem. Eng. Data* **1979**, *24*, 230.

(7) Mussini, T.; Covington, A. K.; Cicognini, M.; Longhi, P.; Rondinini, S. *Anal. Chim. Acta* **1984**, *162*, 103.

(8) Mussini, T.; Covington, A. K.; Longhi, P.; Rondinini, S.; Tettamanti, M. *Anal. Chim. Acta* **1985**, *174*, 331.

(9) Rondinini, S.; Nese, A. *Electrochim. Acta* **1987**, *32*, 1499.

(10) Longhi, P.; Mussini, P. R.; Mussini, T.; Rondinini, S. *J. Solution Chem.* **1988**, *17*, 417.

(11) Ives, D. J. G.; Janz, G. J. *Reference Electrodes*; Academic: New York, 1961; pp 204, 207.

(12) Mussini, T.; Pagella, A. *J. Chem. Eng. Data* **1971**, *16*, 49.

(13) Bates, R. G. *Determination of pH*; Wiley: New York, 1973; p 282.

(14) Mussini, P. R. Thesis, University of Milan, 1986.

(15) Sankar, M.; Macaskill, J. B.; Bates, R. G. *J. Solution Chem.* **1979**, *8*, 887.

(16) Patterson, A.; Felsing, W. A. *J. Am. Chem. Soc.* **1942**, *64*, 1478.

(17) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworths: London, 1965; pp 457, 458.

(18) Washburn, E. W., Ed. *International Critical Tables*, 1st ed.; McGraw-Hill: New York, 1928; Vol. III, pp 27, 115-125.

(19) Äkerlöf, G. *J. Am. Chem. Soc.* **1932**, *54*, 4125.

(20) Hamer, W. J.; Pinching, G. D.; Acree, S. F. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1945**, *35*, 539.

(21) Owen, B. B. *J. Am. Chem. Soc.* **1932**, *54*, 1758.

(22) Marcus, Y. *Pure Appl. Chem.* **1983**, *55*, 977.

(23) Longhi, P.; Mussini, T.; Rondinini, S. *Anal. Chem.* **1986**, *58*, 2290.

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Solubility of Ethylene in *n*-Eicosane, *n*-Octacosane, and *n*-Hexatriacontane

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A semiflow gas absorption equilibrium apparatus is used to measure the solubility of ethylene in three paraffins (*n*-eicosane, *n*-octacosane, and *n*-hexatriacontane) at five pressures (10, 20, 30, 40, and 50 atm) and three temperatures (100, 200, and 300 °C).

Introduction

The three-phase slurry reactor has received much interest as being an effective reactor for the Fischer-Tropsch (F-T) synthesis (*1*). In this type of reactor the catalyst is suspended in a heavy molten wax and the synthesis gas is bubbled through the slurry. Several researchers (*2-4*) have found that the solubilities of the synthesis gases in the slurry were needed for interpretation of the reaction kinetics and for reactor design.

In this work we determined the solubility of ethylene, one of the F-T synthesis products, in three high molecular weight *n*-paraffins as model compounds of F-T wax: *n*-eicosane (*n*-C_{20}), *n*-octacosane (*n*-C_{28}), and *n*-hexatriacontane (*n*-C_{36}). A semiflow vapor-liquid equilibrium apparatus was used to obtain the data under F-T synthesis conditions, 100-300 °C and 10-50 atm.

Experimental Section

The semiflow solubility apparatus and operating procedure used in this work have been described by Huang et al. (*5*). Ethylene gas supplied from a cylinder is bubbled through a presaturator and an equilibrium cell in series while both are filled with a molten wax. The cells are contained in a thermostated nitrogen bath. After allowing sufficient time for equilibration, a

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