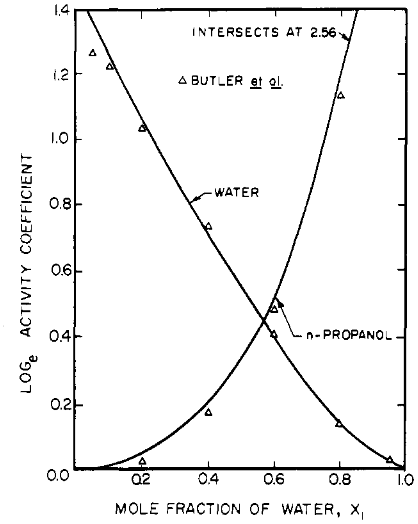

Figure 5. Activity coefficients for the water–propanol system at 298.15 K vs. the liquid mole fraction of water.

agreement is poor. However, in Figure 4 their *x–y* data are seen to be generally in good agreement with the results reported here. Thus, we conclude that their *P–x–y* data are inconsistent and that their pressure measurements are probably in error. Butler et al. (*4*) report activity coefficients for this system at 298.15 K. Their values are shown in Figure 5 compared with the activity coefficients calculated by using the Renon constants from Table V. The agreement is excellent.

Although corrections were made to P_1^s and P_2^s as given by eq 2 and 3, the corrections are very small and need not be made for any practical use of these data. At the maximum temperature of 325 K the use of P_1^s and P_2^s without correction resulted in a total pressure difference in eq 1 of about 0.3 torr or 0.2% and a resultant effect on y_1 of less than 0.001 mole fraction. Thus for practical use of the data, smoothed values of *P–x–y* at any desired temperature can easily be found and therefore are not included here.

Conclusions

The current trend of determining vapor liquid equilibria by measuring only *P–x* data has been used here to slightly lower pressures than normally reported. This has been accomplished by using a differential pressure gauge with the reference side evacuated at low pressures. We have found that adequate degassing is essential at these low pressures and suggest that large errors encountered in reported vapor pressure measurements are attributed primarily to inadequate degassing.

Glossary

B_{ii}	second virial coefficient of component *i*
B_{ij}	second virial interaction coefficient of components *i* and *j*
g_{12}	Gibbs energy parameter defined by eq 7
g^E	molar excess Gibbs energy
P	total pressure of the system
$P_i^{s'}$	"corrected" vapor pressure of component *i*
R	universal gas constant
T	temperature of system
V_i^L	liquid molar volume of component *i*
x_i	liquid mole fraction of component *i*
y_i	vapor mole fraction of component *i*
γ_i	activity coefficient of component *i*
δ_{12}	interaction coefficient defined by eq 4
τ_{ij}	parameter related to the nonrandomness of a mixture in the Renon equation

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Interfacial Tension Measurements for $HClO_4$ Solutions at the Mercury Electrode

Hugues Menard, Bertrand Dubreuil, and Frank M. Kimmerle*

Department of Chemistry, Universitê de Sherbrooke, Sherbrooke, Quebec J1K 2R1, Canada

The interfacial tension at the mercury/perchloric acid interface was determined by the polarographic drop-time method for $HClO_4$ concentrations from 10^{-3} to 1.0 M. The experimental data are presented in the form of fourth-order polynomial expressions and E^{pzc}, the potential, and γ^{pzc}, the interfacial tension at the point of zero charge, are tabulated. Appropriate mathematical treatment of these data allows calculations of double-layer parameters including the cationic and ionic surface excesses presented here.

Experimental Section

All solutions were prepared by dilution from bidistilled water and 70% Matheson Coleman Grade ACS perchloric acid, and their concentrations were verified by acid–base titrations. The solutions were deoxygenated by bubbling nitrogen, which had been previously passed through ammonium metavanadate and water traps, through them. Mallinckrodt "Triple distilled" mercury was vacuum distilled three times before use. All data were obtained at 25 ± 1 °C according to previously published techniques.

Interfacial tension measurements using the procedure described by Mênard and Kimmerle (*1*) based on the polarographic drop-time technique used a 0.1 M KCl reference solution $\gamma^{pzc} = 426.2$ mJ m^{-1} (*2*). The potentials applied to the dropping mercury electrode were measured against a saturated calomel reference SCE electrode. $E_{ClO_4^-}{}^{SCE}$ (the potential between the SCE and an anion-sensitive electrode, ORION Model 92-81) and $E_{H^+}{}^{SCE}$ (the potential between the SCE and a reversible hydrogen

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Table I. Parameter of the Electrocapillary Curves

$[HClO_4]$, M	polynomial coefficients *a*	*b*	*c*	*d*	*e*	γ^{pzc}, mJ m^{-2}	$E_{SCE}{}^{pzc}$, V	$E_{H^+}{}^{pzc}$, V	$E_{ClO_4^-}{}^{pzc}$, V
0.00099	427.15	−0.91	−60.49	−17.5	−86.2	427.2	−0.411	0.000	−0.578
0.00198	426.988	−4.89	−77.41	−42.41	−69.4	427.1	−0.419	−0.028	−0.568
0.0049	426.511	−14.05	−99.18	−36.15	−23.4	427.0	−0.421	−0.053	−0.546
0.0099	426.143	−17.80	−119.24	−67.03	46.3	426.8	−0.432	−0.082	−0.539
0.0198	425.277	−26.88	−121.16	−19.88	15.7	426.8	−0.437	−0.102	−0.522
0.0487	424.140	−35.66	−135.19	−14.17	55.8	426.5	−0.449	−0.130	−0.512
0.099	422.433	−45.78	−147.86	−6.57	83.2	425.9	−0.466	−0.158	−0.508
0.198	420.318	−54.47	−141.46	24.04	76.5	425.4	−0.481	−0.185	−0.500
0.487	415.954	−67.45	−134.34	35.1	41.4	424.0	−0.509	−0.228	−0.498
0.990	411.351	−77.32	−123.42	28.0	−19.2	422.7	−0.549	−0.281	−0.506

Table II. Comparison of γ^{pzc} and $E_{H^+}{}^{pzc}$ Values

$[HClO_4]$, M	interfacial tension γ^{pzc}, mJ m^{-2}			potential of zero charge $E_{H^+}{}^{pzc}$		
	a	*b*	*c*	*a*	*b*	*c*
0.0010	427.2			0.000		
0.0020	427.1			−0.028		
0.0049	427.0			−0.053		
0.010	426.8			−0.082		−0.086
0.011		425.3			−0.085	
0.020	426.8			−0.102		
0.027		425.2			−0.1150	
0.049	426.5			−0.130		
0.054		425.0			−0.1396	
0.10	426.0	425.2[d]	426.0	−0.158		−0.160
0.11		424.7			−0.1644	
0.20	425.5			−0.185		
0.22		423.9			−0.1928	
0.49	424.1			−0.228		
0.54		422.5			−0.2367	
0.93		421.4			−0.2672	
1.0	422.7			−0.281		−0.273
1		419.3			−0.3204	
3.7		416.4			−0.407	

[a] This work. [b] Reference 4. [c] Reference 6. [d] Reference 5.

electrode) were recorded in separate experiments. The potential of zero charge was determined by the streaming jet electrode according to the method described by Kimmerle and Mênard (*3*).

Results and Discussions

The electrocapillary curve $\gamma = f(E_{H^+},[HClO_4])$ can be represented as a polynomial expression

$$\gamma = a + bE_{H^+} + c(E_{H^+})^2 + d(E_{H^+})^3 + e(E_{H^+})^4 \quad (1)$$

(mJ m^{-2}), E_{H^+} is the electrode potential measured with respect to a reversible hydrogen electrode, and *a*, *b*, *c*, *d*, and *e* are the polynomial coefficients shown in columns 2-6 of Table I. Also given in Table I are the interfacial tension at the point of zero charge, γ^{pzc}, and the potential at the point of zero charge measured with respect to a saturated calomel electrode, $E_{SCE}{}^{pzc}$, a reversible hydrogen electrode, $E_{H^+}{}^{pzc}$, and a perchlorate selective electrode $E_{ClO_4^-}{}^{pzc}$.

The $E_{SCE}{}^{pzc}$ agree to within 2 mV with the values measured with the streaming electrode and reproduced in Table II. General agreement exists between the $E_{H^+}{}^{pzc}$ values quoted by various workers. Our γ values are about 1 mJ m^{-2} higher than those reported by Parsons and Payne (*4*). Since their values were calculated by using a Lippman capillary electrometer and ours were obtained by the drop-time technique, this agreement is also satisfactory. We believe our data to be reproducible to within 0.1 mJ m^{-2} near the pcz and to within 0.2 mJ m^{-2} near the extremities of the electrocapillary curve, i.e., precise enough to permit detailed calculations of double-layer parameters.

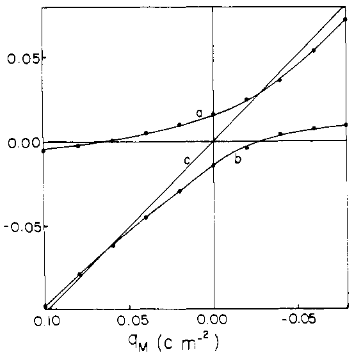

Figure 1. Ionic surface excess values vs. electrode charge for a 0.1 M $HClO_4$ solution curve: (a) $F\Gamma_{H^+}$; (b) $-F\Gamma_{ClO_4^-}$; (c) q_S calculated from eq 2, 3, and 5, respectively.

Cationic surface excess values were calculated according to the expression

$$\Gamma_{H^+} = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln a_{HClO_4}}\right)_{E(ClO_4^-)} \quad (2)$$

anionic surface excess values according to the expression

$$\Gamma_{ClO_4^-} = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln a_{HClO_4}}\right)_{E(H^+)} \quad (3)$$

and the electrical charge on the metal according to the expression

$$q_M = -\left(\frac{\partial\gamma}{\partial E_{SCE}}\right)_{\mu(HClO_4)} = -\left(\frac{\partial\gamma}{\partial E_{H^+}}\right)_{\mu(HClO_4)} = -\left(\frac{\partial\gamma}{\partial E_{ClO_4^-}}\right)_{\mu(HClO_4)} \quad (4)$$

where the activities, a_{HClO_4}, were interpolated from the data of Butler (*5*) and of Robinson (*7*) and where the potentials were calculated as described above.

The independently determined ionic excess values, Γ_{H^+} and $\Gamma_{ClO_4^-}$, provided a check on the computational technique. As curve c of Figure 1 indicates, the ionic charge in solution

$$q_S = F(\Gamma_{H^+} - \Gamma_{ClO_4^-}) \quad (5)$$

varies linearly with the excess electric charge on the metal, q_M. The experimentally determined ratio $q_S/q_M = -1.016 \pm 0.004$ for a 0.05 M $HClO_4$ solution. At negatively charged surfaces ($q_M < 0.03$ C m^{-2}) $\Gamma_{ClO_4^-} < 0$; i.e., the perchlorate ion is repelled from the surface. At positively charged surfaces ($q_M > 0.05$ C m^{-2}) $\Gamma_{H^+} < 0$; i.e., the proton is slightly repelled from the surface. At $q_M = 0$ where the simple electrostatic theory would predict $\Gamma_{H^+} = \Gamma_{ClO_4^-} = 0$, we find $F\Gamma_{H^+} = F\Gamma_{ClO_4^-} = 0.12$ C m^{-2};

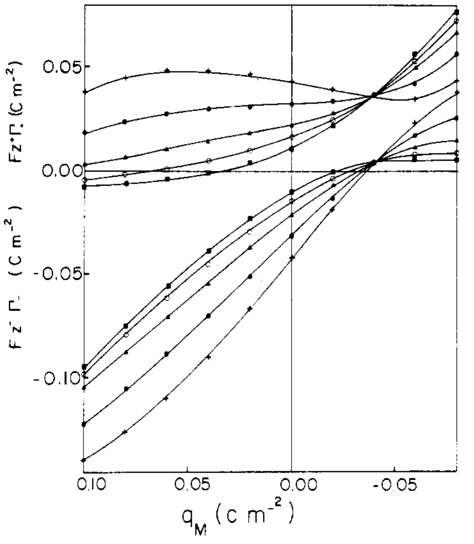

Figure 2. Ionic surface excess values vs. electrode charge, calculated as for Figure 1. [$HClO_4$] = (■) 0.05 M, (O) 0.1 M, (▲) 0.2 M, (●) 0.5 M, (+) 1.0 M.

i.e., a slight nonelectrostatic attraction of the ionic species to the surface.

Figure 2 represents the variation of the $F\Gamma_{H^+}$ and $F\Gamma_{ClO_4^-}$ values as calculated according to eq 2 and 3, respectively, with surface charge and electrolyte concentration. At the lowest concentrations ([$HClO_4$] < 0.05 M) the results approach the behavior predicted by the electrostatic model and observed for NaF solutions. At higher concentrations the nonelectrostatic attraction between the perchlorate ion and the electrode surface manifests itself by the higher than predicted Γ_{H^+} and $\Gamma_{ClO_4^-}$ values.

Acknowledgment

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Thermal Conductivity of Water and Oleum

J. E. S. Venart* and R. C. Prasad

Department of Mechanical Engineering, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3

The paper reports measurements of the thermal conductivity of nominal 30, 39, and 65% oleum in the temperature range 20–50 °C at 0.1 MPa, performed by means of an absolute transient line-source technique. It is estimated that the overall uncertainty in the thermal conductivity data is less than ±1.5% on the basis of water measurements over the temperature range 0–95 °C.

Introduction

As part of a program in the evaluation of new heat exchanger performance, data on the thermal conductivity of oleum were required (*1*). Thermal conductivity measurements for sulfuric acid are few (*2*, *3*) and there appears to be none for oleum.

A precise determination of thermal conductivity for such a fluid is extremely difficult because of its strong reactivity, particularly its hydroscopic and ionic effects. Measurements are reported of the thermal conductivity of 30.5, 38.8, and 65.6% free SO_3 oleum in the temperature range 20-50 °C at 0.1 MPa performed by means of an absolute transient line-source technique. It is estimated that overall uncertainty on the thermal conductivity data is less than ±1.5% on the basis of cocurrent measurements on water over the temperature range 0-95 °C. Thirty-two measurements on the oleum samples and twenty-two measurements on distilled, demineralized water are reported.

Experimental Section

The measurements were performed with the transient hot-wire apparatus which has been described elsewhere (*4*, *5*). The instrument was used without major modification for the measurements reported here although there were some differences in the cell construction, cell thermostat, and experimental procedures, which were required for oleum; they will be described later.

In the transient line source method, a fine metal wire (typically 5–100 μm) immersed vertically in the fluid, and contained in a cylindrical enclosure initially at thermal equilibrium, is heated electrically from zero time. The device to a first approximation simulates an infinite line source of constant heat generation. The temperature rise at the wire surface in a time t_1 to t_2 is

$$\Delta T_W = \frac{Q_l}{4\pi\lambda} \ln\left(\frac{t_2}{t_1}\right) \quad \text{for } \frac{\alpha t}{a^2} > 30 \qquad (1)$$

where Q_l is the heat generated per unit length of wire of radius a. Equation 1 does not depend on the thermal diffusivity, α,