the highest NaCl concentration, for example, in 4 m NaCl at 250 °C and 3 and 4 m NaCl at 300 °C.

Registry No. $BaSO_4$, 7727-43-7; NaCl, 7647-14-5.

Literature Cited

(1) Hanor, J. S. Ph.D. Thesis, Harvard University, 1966.
(2) Fresenius, R.; Hintz, E. Z. *Anal. Chem.* **1896**, *35*, 170.
(3) Fraps, G. S. *Am. Chem. J.* **1902**, *27*, 288.
(4) Rosseinsky, D. R. *Trans. Faraday Soc.* **1956**, *104*, 116.
(5) Ghosh, S. C.; Sarkar, A.; Mukherjee, S. K. *J. Indian Chem. Soc.* **1969**, *46*, 784.
(6) Kritsotakis, K. *Fortschr. Mineral.* **1974**, *52*, 41.
(7) Melcher, A. C. *J. Am. Chem. Soc.* **1910**, *32*, 50.
(8) Neuman, E. W. *J. Am. Chem. Soc.* **1933**, *55*, 879.
(9) Templeton, C. C. *J. Chem. Eng. Data* **1980**, *5*, 514.
(10) Selivanova, N. M.; Kapustinskii, A. F. *Zh. Fiz. Khim.* **1953**, *27*, 565.
(11) Burton, J. D.; Marshall, N. J.; Phillips, A. J. *Nature* **1968**, *217*, 834.
(12) Davies, J. A.; Collins, G. A. *Environ. Sci. Technol.* **1971**, *5*, 1039.
(13) Luccesi, P. J.; Whitney, E. D. *J. Appl. Chem.* **1962**, *12*, 277.
(14) Strubel, G. *Neues. Jahrb. Mineral. Monatsh.* **1967**, 223.
(15) Blount, C. W. *Am. Mineral.* **1977**, *62*, 942.
(16) Khodakovskiy, I. L.; Mishin, I. V.; Zhogina, V. V. *Geokhimiya* **1966**, *7*, 861.
(17) Barton, P. W. *Econ. Geol.* **1957**, *52*, 333.
(18) Egorov, A. M.; Titova, Z. P. *Russ. J. Inorg. Chem.* **1962**, *7*, 141.
(19) Malinin, S. D.; Uchameyshvili, N. Ye.; Khitarov, N. I. *Geokhimiya* **1969**, *8*, 927.
(20) Uchameyshvili, N. Ye.; Malinin, S. D.; Khitarov, N. I. *Geokhimiya* **1966**, *10*, 1193.
(21) Rogers, P. S. Z. Ph. D. Thesis, University of California, Berkeley, 1980.
(22) Pitzer, K. S. In *Activity Coefficients in Electrolyte Solutions*; Pytkowicz, R. M., Ed.; CRC: Boca Raton, FL, 1979; Vol. 1, Chapter 7.
(23) Kelley, K. K. *U.S. Bur. Mines Bull.* **1960**, No. 476.
(24) (a) Barin, I.; Knacke, O. *Thermochemical Properties of Inorganic Substances*; Springer-Verlag: Berlin, 1973. (b) Barin, I.; Knack, O.; Kubaschewski, O. *Thermochemical Properties of Inorganic Substances*; Springer-Verlag: Berlin, 1977; Supplement.
(25) Barner, H. E.; Scheuerman, R. V. *Handbook of Thermochemical Data for Compounds and Aqueous Species*; Wiley: New York, 1978.
(26) Parker, V. B.; Wagman, D. D.; Evans, W. H. *NBS Tech. Note* **1971**, No. 270-6.
(27) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttal, R. L. *J. Phys. Chem. Ref. Data* **1982**, 11, Suppl. No. 2.
(28) Helgeson, H. C. *Am. J. Sci.* **1969**, *267*, 729.
(29) Criss, C. M.; Cobble, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 5385, 5390.
(30) Debye, P.; Hückel, E. *Phys. Z.* **1923**, *24*, 185.
(31) Pitzer, K. S. *J. Phys. Chem.* **1973**, *77*, 268.
(32) Pitzer, K. S.; Mayorga, G. *J. Phys. Chem.* **1973**, *77*, 2300.
(33) Pitzer, K. S.; Mayorga, G. *J. Solution Chem.* **1973**, *3*, 539.
(34) Pitzer, K. S.; Kim, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 5701.
(35) Pitzer, K. S. *J. Solution Chem.* **1975**, *4*, 249.
(36) Pitzer, K. S.; Silvester, L. F. *J. Solution Chem.* **1976**, *5*, 269.
(37) Khoo, K. H.; Chan, C. Y.; Lim, T. K. *J. Solution Chem.* **1977**, *6*, 855.
(38) Khoo, K. H.; Chan, C. Y.; Lim, T. K. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2037.
(39) Boyd, G. E. *J. Solution Chem.* **1977**, *6*, 135.
(40) White, D. R. Jr.; Robinson, R. A.; Bates, R. G. *J. Solution Chem.* **1980**, *9*, 457.
(41) Macaskill, J. B.; White, D. R. Jr.; Robinson, R. A.; Bates, R. G. *J. Solution Chem.* **1978**, *7*, 339.
(42) Roy, R. N.; Gibbons, J. J.; Bliss, D. P. Jr.; Casebolt, R. G.; Baker, B. K. *J. Solution Chem.* **1980**, *9*, 911.
(43) Ananthaswamy, J.; Atkinson, G. *J. Solution Chem.* **1982**, *11*, 509.
(44) Kumar, A.; Atkinson, G.; Howell, R. D. *J. Solution Chem.* **1982**, *11*, 857.
(45) Ananthasway, J.; Atkinson, G. *J. Chem. Eng. Data* **1985**, *30*, 120.
(46) Hanna, T. M.; Atkinson, G. *J. Phys. Chem.* **1985**, *89*, 4884.
(47) Usha, A. V.; Raju, K.; Atkinson, G. *J. Phys. Chem.* **1987**, *91*, 4796.
(48) Harvie, C. E.; Weare, J. H. *Geochim. Cosmochim. Acta* **1980**, *44*, 981.
(49) Harvie, C. E.; Eugster, H. P.; Weare, J. H. *Geochim. Cosmochim. Acta* **1982**, *46*, 1603.
(50) Holmes, H. F.; Mesmer, R. E. *J. Chem. Thermodyn.* **1983**, *15*, 709.
(51) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97.
(52) Akerlof, G. C.; Oshry, H. I. *J. Am. Chem. Soc.* **1950**, *72*, 2844.
(53) Rogers, P. S. Z.; Pitzer, K. S. *J. Phys. Chem.* **1981**, *85*, 2886.
(54) Pitzer, K. S.; Peiper, J. C.; Bisey, R. H. *J. Phys. Chem. Ref. Data* **1984**, *13*, 1.

Received for review October 15, 1987. Accepted May 11, 1988. This research was supported by a consortium of 11 major oil production and service companies.

Apparent Molal Volumes and Heat Capacities of Aqueous HCl and $HClO_4$ at 15–55 °C

Randall Pogue and Gordon Atkinson*

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019

The apparent molal volumes and apparent molal heat capacities of dilute (0.01–0.25 m) aqueous HCl and $HClO_4$ solutions have been determined at 15, 25, 35, 45, and 55 °C. These apparent molal quantities have been extrapolated to zero concentration to obtain the limiting values at infinite dilution, which are the same as the infinite dilution partial molal values. The apparent molal quantities were fitted with the equation $\phi_J = \phi_J{}^0 + A_J m^{1/2} + B_J m$. Taking $\phi_J{}^0(H^+) = 0$, conventional ionic $\phi_J{}^0$'s are obtained for the Cl^- and ClO_4^- anions at each temperature.

Introduction

The apparent molal properties of HCl and $HClO_4$ at 25 °C are well-known. The data become ambiguous and scattered at temperatures other than 25 °C. We have determined values of $\phi_V{}^0$ and $\phi_{C_p}{}^0$ at 15, 25, 35, 45, and 55 °C for both HCl and $HClO_4$. These results are important since we use the standard convention and set $\phi_J{}^0(H^+) = 0$ at all temperatures; thus the acid values yield the conventional anion values. These anion values are then used to calculate other ionic values from salt data. Any error in these original anion values is propagated throughout subsequent calculations of ionic $\phi_J{}^0$'s. Determination of these anion $\phi_J{}^0$'s will provide a consistent data base from which all other ionic $\phi_J{}^0$ values can be calculated in later work.

Experimental Section

The densities were measured with a Paar Mettler DMA 602 vibrating tube densimeter and the heat capacities with a Sodev flow calorimeter. The densimeter was calibrated with NaCl solutions by using the data of Millero (*1*). The operation of a vibration tube densimeter has been previously described (*2*). The calorimeter performance was verified with NaCl solutions against the data of Desnoyers (*3*). Both measurements were carried out at 15, 25, 35, 45, and 55 °C. The densimeter cell temperature was controlled to within ±0.005 °C with an accuracy of 0.001 °C by using a miniature PRT and a Neslab bath combination. The calorimeter cell temperature was maintained within ±0.005 °C and an accuracy of 0.05 °C with a closed loop circulation system Model CT-L provided by Sodev. The values of the density and heat capacity of pure water used

0021-9568/88/1733-0495$01.50/0

Table I. Relative Densities and Apparent Molal Volumes (AMV's) and Apparent Molal Heat Capacities of Aqueous HCl and $HClO_4$ Solutions

Densities and AMV's

molality, mol kg^{-1}	1000(RD), g cm^{-3}	ϕ_v, cm^3 mol^{-1}	molality, mol kg^{-1}	1000(RD), g cm^{-3}	ϕ_v, cm^3 mol^{-1}	molality, mol kg^{-1}	1000(RD), g cm^{-3}	ϕ_v, cm^3 mol^{-1}
				HCl				
				288.15 K				
0.01005	0.192	17.32	0.05050	0.947	17.58	0.1240	2.297	17.89
0.02032	0.388	17.42	0.07539	1.407	17.72	0.1488	2.753	17.92
0.03001	0.570	17.46	0.1001	1.864	17.81	0.2303	4.228	18.03
				298.15 K				
0.01005	0.186	17.92	0.05050	0.921	18.20	0.1240	2.241	18.34
0.02032	0.373	18.06	0.07539	1.372	18.23	0.1488	2.685	18.37
0.03001	0.551	18.06	0.1001	1.814	18.30	0.2303	4.125	18.48
				308.15 K				
0.01005	0.183	18.25	0.05050	0.911	18.41	0.1240	2.224	18.52
0.02032	0.372	18.19	0.07539	1.340	18.45	0.1488	2.661	18.56
0.03001	0.540	18.38	0.1001	1.795	18.47	0.2303	4.089	18.66
				318.15 K				
0.01005	0.186	17.94	0.05050	0.908	18.47	0.1240	2.199	18.69
0.02032	0.369	18.29	0.07539	1.351	18.52	0.1488	2.637	18.70
0.03001	0.543	18.36	0.1001	1.787	18.58	0.2303	4.052	18.80
				328.15 K				
0.01005	0.188	17.83	0.05050	0.921	18.31	0.1240	2.227	18.53
0.02032	0.378	17.99	0.07539	1.365	18.40	0.1488	2.663	18.59
0.03001	0.556	18.05	0.1001	1.769	18.44	0.2303	4.080	18.73
				$HClO_4$				
				288.15 K				
0.00987	0.577	41.99	0.05050	2.915	42.60	0.1528	8.746	42.83
0.01996	1.160	42.32	0.07559	4.351	42.70	0.2165	12.348	42.88
0.02977	1.724	42.46	0.1006	5.775	42.79			
				298.15 K				
0.00987	0.554	44.20	0.05050	2.820	44.44	0.1528	8.480	44.53
0.01996	1.119	44.30	0.07559	4.217	44.44	0.2165	11.982	44.55
0.02977	1.665	44.39	0.1006	5.604	44.47			
				308.15 K				
0.00987	0.541	45.65	0.05050	2.747	45.89	0.1528	8.264	45.93
0.01996	1.088	45.84	0.07559	4.107	45.88	0.2165	11.670	45.98
0.02977	1.624	45.80	0.1006	5.458	45.90			
				318.15 K				
0.00987	0.531	46.77	0.05050	2.686	47.06	0.1528	8.071	47.18
0.01996	1.069	46.79	0.07559	4.010	47.12	0.2165	11.394	47.24
0.02977	1.590	46.92	0.1006	5.328	47.18			
				328.15 K				
0.00987	0.517	47.91	0.05050	2.634	48.10	0.1528	7.907	48.25
0.01996	1.046	47.91	0.07559	3.931	48.19	0.2165	11.174	48.25
0.02977	1.555	48.05	0.1006	5.221	48.24			

Apparent Molal Heat Capacities

molality, mol kg^{-1}	c_p, J K^{-1} g^{-1}	ϕ_c, J K^{-1} mol^{-1}	molality, mol kg^{-1}	c_p, J K^{-1} g^{-1}	ϕ_c, J K^{-1} mol^{-1}	molality, mol kg^{-1}	c_p, J K^{-1} g^{-1}	ϕ_c, J K^{-1} mol^{-1}
				HCl				
				288.15 K				
0.05012	4.1716	−132.0	0.1150	4.1543	−122.5	0.1496	4.1449	−122.6
0.07491	4.1648	−127.9	0.1246	4.1515	−124.3	0.2303	4.1233	−121.0
				298.15 K				
0.05012	4.1661	−117.6	0.1150	4.1492	−113.5	0.1496	4.1403	−111.9
0.07591	4.1596	−114.9	0.1246	4.1467	−113.0	0.2303	4.1197	−110.1
				308.15 K				
0.05012	4.1653	−105.6	0.1150	4.1491	−101.4	0.1496	4.1407	−100.0
0.07491	4.1591	−103.0	0.1246	4.1467	−101.3	0.2303	4.1212	−97.4
				318.15 K				
0.05012	4.1672	−92.5	0.1150	4.1520	−87.7	0.1496	4.1438	−87.8
0.07491	4.1616	−87.8	0.1246	4.1499	−86.1	0.2303	4.1254	−84.3
				328.15 K				
0.05012	4.1701		0.1150	4.1554	−83.6	0.1496	4.1475	−82.3
0.07491	4.1650	−80.6	0.1246	4.1532	−83.0	0.2303	4.1289	−81.6

Table I (Continued)

Apparent Molal Heat Capacities								
molality, mol kg^{-1}	c_p, J K^{-1} g^{-1}	ϕ_c, J K^{-1} mol^{-1}	molality, mol kg^{-1}	c_p, J K^{-1} g^{-1}	ϕ_c, J K^{-1} mol^{-1}	molality, mol kg^{-1}	c_p, J K^{-1} g^{-1}	ϕ_c, J K^{-1} mol^{-1}
				$HClO_4$				
				288.15 K				
0.04949	4.1636	-30.0	0.1006	4.1412	-27.4	0.1481	4.1213	-21.4
0.07575	4.1518	-32.0	0.1243	4.1312	-24.3	0.2165	4.0931	-16.8
				298.15 K				
0.04949	4.1583	-13.6	0.1006	4.1376	-1.6	0.1481	4.1180	-2.1
0.07575	4.1476	-5.9	0.1243	4.1273	-6.0	0.2165	4.0918	5.6
				308.15 K				
0.04949	4.1576	2.3	0.1006	4.1372	7.8	0.1481	4.1180	7.2
0.07575	4.1472	7.5	0.1243	4.1280	10.6	0.2165	4.0923	14.2
				318.15 K				
0.04949	4.1595	14.5	0.1006	4.1398	21.4	0.1481	4.1213	21.3
0.07575	4.1492	16.9	0.1243	4.1307	22.2	0.2165	4.0960	25.7
				328.15 K				
0.04949	4.1633	33.2	0.1006	4.1448	42.1	0.1481	4.1264	36.2
0.07575	4.1536	37.3	0.1243	4.1355	37.9	0.2165	4.1026	43.4

during calibration and in the following calculations were those of Kell (*4*) and Osborne (*5*).

Stock solutions of perchloric acid and hydrochloric acid were prepared from reagent grade concentrated acids. The stock solutions were titrated versus aqueous NaOH that had been standardized by titration versus potassium hydrogen phthalate. All analyses were within ±0.05%. The stock solutions, as well as solutions for measurement, were prepared with 18.5 mΩ cm^{-1} deionized water. Solutions for measurements were prepared by weight dilution of the corresponding stock solutions.

Results and Calculations

The Sodev flow calorimeter measures heat capacities per unit volume. In order to calculate the apparent molal heat capacities one must know the solution densities. The densities serve the dual purpose of providing the apparent molal volumes and permitting the calculation of the apparent molal heat capacities.

The apparent molal volumes, ϕ_v, have been calculated from solution densities d, by the equation

$$\phi_v = (M_2/d) - 1000(d - d_0)/mdd_0 \qquad (1)$$

Similarly, apparent molal heat capacities, ϕ_c, are calculated from

$$\phi_c = (M_2 c_p) + 1000(c_p - c_{p_0})/m \qquad (2)$$

Symbols in these equations have the following meanings: c_p and c_{p_0} are the heat capacities of solution and pure water expressed in terms of J K^{-1} g^{-1}, d is the density (g/cm^3) of a solution of molality m, d_0 is pure water density, and M_2 is the solute molecular weight. The density data were fitted with a polynomial which was then used to calculate the densities of the solutions used to measure the apparent molal heat capacities. The error in the calculated density values was <3 ppm. The apparent molal heat capacities and volumes calculated from eq 1 and 2 are listed in Table I.

Our ϕ_J values for both electrolytes can be accurately described by an equation of the form

$$\phi_J = \phi_J^0 + S_J m^{1/2} + B_J m \qquad (3)$$

in which ϕ_J^0 represents the value of ϕ_J at infinite dilution. S_J is the theoretical Debye–Hückel limiting slope, m is the molality, and B_J is an adjustable parameter. Our principal purpose in this work has been to determine a consistent set of ϕ_J^0 values at each temperature. We have fitted our volume and heat capacity data to eq 3 with a weighted nonlinear least-squares fit, the weighting proportional to $(1/\sigma_{\phi_J})$. See Figures 1 and 2. The resulting ϕ_v^0 and ϕ_c^0 values at each temperature are listed in Table II with the corresponding Debye–Hückel slopes.

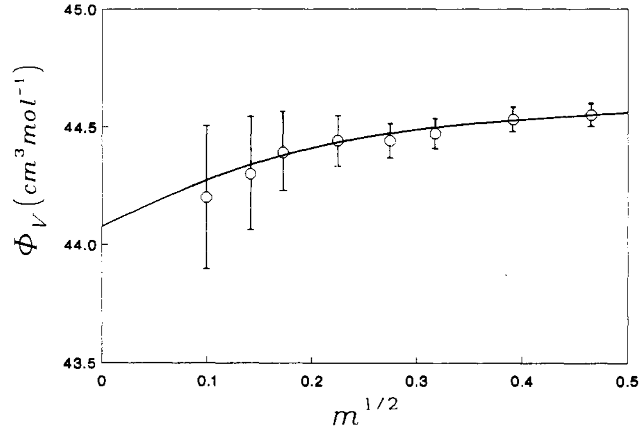

Figure 1. Plot of ϕ_v vs $m^{1/2}$ for $HClO_4$ at 25 °C. Illustrates weighted NLLSQ fit with error bars.

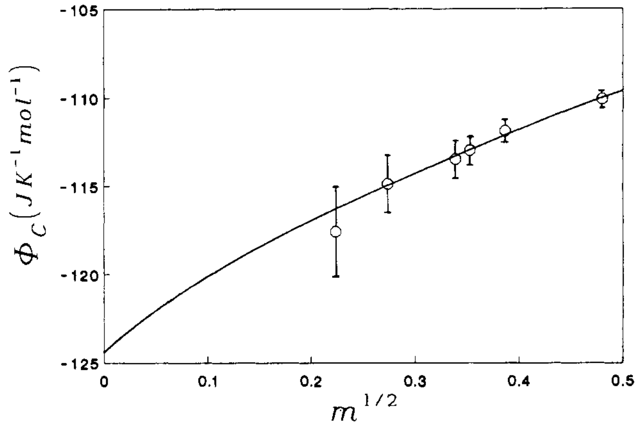

Figure 2. Plot of ϕ_c vs $m^{1/2}$ for HCl at 25 °C.

Our results for ϕ_v^0(HCl) are in good agreement with the work of Millero et al. (*6*) and Herrington et al. (*7*) at all temperatures, as shown in Table III. The current literature values of ϕ_v^0 for $HClO_4$ are suspect due to the indirect method used for their determination. Our value, $\phi_v^0(HClO_4)$ = 44.09 cm^3 mol^{-1} at 25 °C, is in good agreement with the 44.12 cm^3 mol^{-1} reported by

Table II. Conventional $\phi_v^0(H^+) = 0$ Ionic Heat Capacities and Volumes of Aqueous Cl^- and ClO_4^- Solutions

T, °C	ϕ_v^0, cm^3 mol^{-1}	b_v, cm^3 kg mol^{-2}	ϕ_c^0, J K^{-1} mol^{-1}	b_c, J kg K^{-1} mol^{-2}
		Cl^-		
15	17.12	0.841	−133.1	−0.315
25	17.80	−0.930	−123.8	−0.814
35	18.00	−1.478	−112.1	−3.157
45	17.99	−1.107	−97.3	−17.794
55	17.74	−0.613	−91.7	−37.700
		ClO_4^-		
15	42.20	−0.282	−40.0	53.183
25	44.09	−1.913	−22.5	64.983
35	45.52	−2.391	−3.9	11.109
45	46.62	−1.867	8.8	1.586
55	47.56	−1.544	24.2	−0.824

Table III. Comparison of Apparent Molal Volumes and Apparent Molal Heat Capacities Obtained in This Study and by Other Workers

T, °C	our results	other workers
		ϕ_v^0, cm^3 mol^{-1}
		HCl
15	17.12	17.43 (*6*)
25	17.80	17.82 (*6*), 18.1 (*10*), 17.83 (*11*), 17.76 (*12*), 17.80 (*7*)
35	18.00	17.96 (*6*), 18.2 (*13*), 18.13 (*7*)
45	17.99	17.84 (*6*), 18.02 (*7*)
55	17.74	17.75 (*7*)
		$HClO_4$
15	42.20	43.03 (*14*)
25	44.09	44.12 (*14*), 44.10 (*7*)
35	45.52	44.75 (*14*), 45.45 (*7*)
45	46.62	45.00 (*14*), 46.36 (*7*)
55	47.56	44.86 (*14*), 47.27 (*7*)
		ϕ_c^0, J K^{-1} mol^{-1}
		HCl
25	−123.8	−123.1 (*8*)
		$HClO_4$
25	−22.5	−27.1 (*9*)

Millero. Our values at other temperatures differ from the results calculated by Millero. The values reported by Herrington show limited agreement but the lowest molality at which they made measurements was 0.25 *m* (see Table III). We suggest that better values were obtained from our direct measurements at each temperature and the theoretical Debye-Hückel slope rather than the Pitzer formalism for extrapolation and determination of ϕ_v^0.

Our present $\phi_c^0(HCl) = -123.82$ J K^{-1} mol^{-1} compares favorably with the −123.1 J K^{-1} mol^{-1} obtained by Desnoyers (*8*). Our $\phi_c^0(HClO_4) = -22.5$ J K^{-1} mol^{-1} is in fair agreement with $\phi_c^0(HClO_4) = -27.1$ J K^{-1} mol^{-1} from Hepler (*9*). Due to the lack of literature data we are unable to make any direct comparisons of our ϕ_c^0 values at 15, 35, 45, and 55 °C for HCl and $HClO_4$.

The limiting values, ϕ_J^0, were fitted to polynomials of the form

$$\phi_J^0 = a + bt + ct^2 + dt^3 \qquad (4)$$

where *t* is the temperature in degrees Celsius. The resulting parameters for each salt are listed in Table IV.

The ϕ_v^0 data for HCl exhibits a maximum at 37.1 °C, which follows the trend of chloride salts showing a maximum ϕ_v^0 value below 60 °C. The $HClO_4$ ϕ_v^0 data show no such maximum in the temperature range studied (see Figures 3 and 4). The data indicate a maximum will occur near 70 °C. The ϕ_c^0 data for both acid systems are similar. The data show an almost linear increase in ϕ_c^0 with temperature (Figure 5). It is not possible with the current data to predict at what temperature a maximum will occur.

Table IV. Parameters for Eq 4

ϕ_v	a, cm^3 mol^{-1}	b, cm^3 mol^{-1} K^{-1}	c, cm^3 mol^{-1} K^{-2}	d, cm^3 mol^{-1} K^{-3}
HCl	15.09	0.184	−0.0036	0.00002
$HClO_4$	38.93	0.244	−0.0016	

ϕ_c	a, J K^{-1} mol^{-1}	b, J K^{-2} mol^{-1}	c, J K^{-3} mol^{-1}
HCl	−153.00	1.308	−0.0031
$HClO_4$	−69.97	2.099	−0.0072

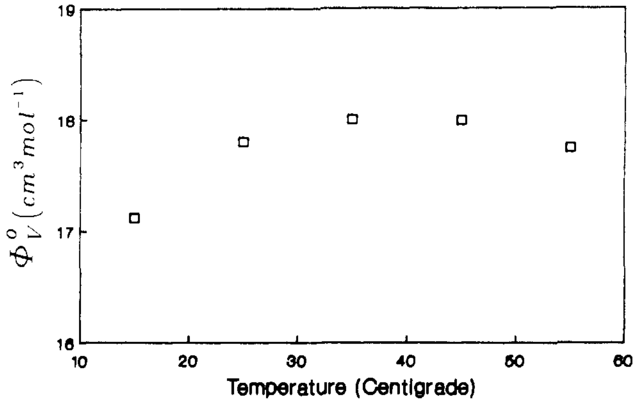

Figure 3. Temperature dependence of ϕ_v^0 for HCl.

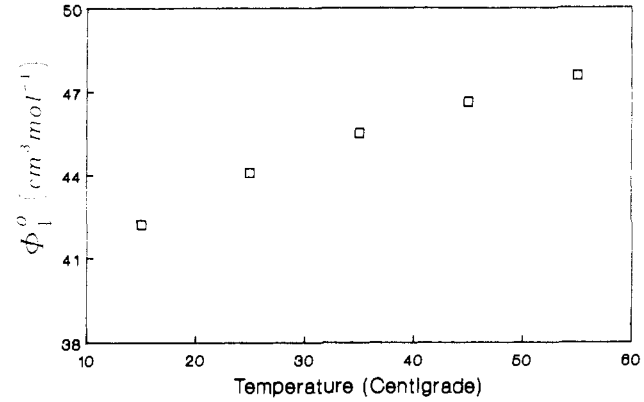

Figure 4. Temperature dependence of ϕ_v^0 for $HClO_4$.

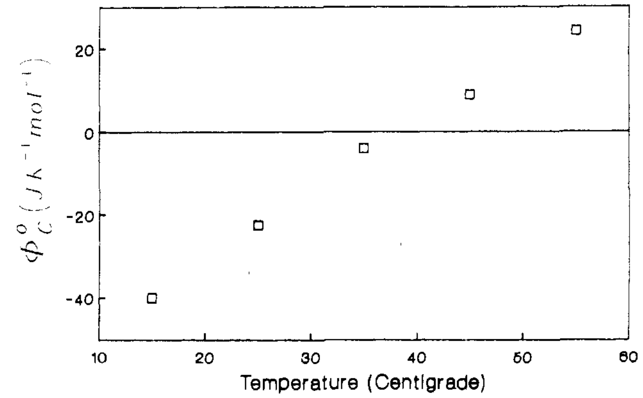

Figure 5. Temperature dependence of ϕ_c^0 for HCl.

Registry No. HCl, 7647-01-0; $HClO_4$, 7601-90-3.

Literature Cited

(1) Chen, C.-T.; Chen, L.-S.; Millero, F. J. *J. Acoust. Soc. Am.* **1978**, *63*, 1795–1800.
(2) Picker, P.; Tremblay, E.; Jolicoeur, C. *J. Solution Chem.* **1974**, *3*, 377.
(3) Perron, G.; Fortier, J.; Desnoyers, J. E. *J. Chem. Thermodyn.* **1975**, *7*, 1177–84.

(4) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97–105.
(5) Osborne, N. S.; Stimson, H. F.; Ginnings, D. C. *J. Res. Natl. Bur. Stand.* **1939**, *23*, 238.
(6) Millero, F. J. *Geochim. Cosmochim. Acta* **1982**, *46*, 11–22.
(7) Herrington, T. M.; Pethybridge, A. D.; Roffey, M. G. *J. Chem. Eng. Data* **1985**, *30*, 284–67.
(8) Forteir, J. L.; Leduc, P. A.; Desnoyers, J. E. *J. Solution Chem.* **1974**, *3*, 323–49.
(9) Singh, P. P.; McCurdy, K. G.; Woolley, E. M.; Hepler, L. G. *J. Solution Chem.* **1977**, *6*, 327–30.
(10) Owen, B. B.; Brinkley, S. R. *Chem. Rev.* **1941**, *29*, 461.
(11) Redlich, O.; Bigeleisen, J. *J. Am. Chem. Soc.* **1942**, *64*, 758.
(12) Owen, B. B.; Brinkley, S. R. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 753.
(13) Fajans, K.; Johnson, O. *J. Am. Chem. Soc.* **1942**, *64*, 668.
(14) Millero, F. J. In *Water and Aqueous Solutions*; Horne, R. A., Ed.; Wiley Interscience: Toronto, 1972; Chapter 13.

Received for review December 16, 1987. Accepted June 13, 1988. This research was supported by DOE Grant De-FG01-87FE61146.

Vapor–Liquid Equilibrium Measurements for Binary Systems of Acetic Acid with Ethyl Acetate and Vinyl Acetate by the Dew–Bubble Point Temperature Method

Masahiro Kato

Department of Industrial Chemistry, Faculty of Engineering, Nihon University, Koriyama, Fukushima 963, Japan

Vapor–liquid equilibrium relations were measured for the binary systems ethyl acetate–acetic acid and vinyl acetate–acetic acid at 740 mmHg pressure by the dew–bubble point temperature method. The dew–bubble point temperature apparatus previously proposed by the authors was modified to reduce the time required for the experiment. To keep the flow rate constant, the construction of the feeder was further modified to maintain the liquid level constant in it. Vapor–liquid equilibrium relationships were obtained for the binary systems by combining the dew point temperature curve and the bubble point one. Large differences are shown among the previous experimental data in the literature for the systems of the present study. The composition analysis seems troublesome for these systems containing acetic acid in the conventional experimental methods. The present experimental method does not require any analytical instrument for the vapor–liquid equilibrium measurements. For the correlation of the experimental data, the Wilson equation was successfully applied, accounting for the association effect of acetic acid in vapor phase.

Introduction

Vapor–liquid equilibrium relations are required for practical use, such as in the design and operation of distillation equipment. In the conventional experimental methods of vapor–liquid equilibria, analytical instruments are required. For measurements of isobaric dew points, a unique vapor-mixing-type apparatus was proposed by Kojima et al. (*1*). For measurement of isobaric bubble points, many researchers (*2–4*) have proposed some ebulliometers. However, in the general batch-type ebulliometer, it is necessary to correct for the difference between the liquid composition at steady state and the feed composition. Kojima et al. (*5*) determined vapor–liquid equilibria of two-liquid-phase systems, combining the dew and bubble points separately measured.

The authors previously proposed two types of apparatus for measuring isobaric dew and bubble points. One is the vapor-mixing type (*6*), and the other is flow type (*7*). In the present work, the flow-type apparatus was further modified. Large differences in the data from the literature are observed for vapor–liquid equilibria of binary systems made of acetic acid and acetate (*8–12*). Vapor–liquid equilibrium relations were measured for the binary systems ethyl acetate–acetic acid and vinyl acetate–acetic acid at 740 mmHg pressure by the dew–bubble point temperature method.

Table I. Physical Properties of Materials Used

material	density at 25 °C, g/cm^3 exptl	density at 25 °C, g/cm^3 lit.	normal bp, °C exptl	normal bp, °C lit.
acetic acid	1.0437	1.04365 (*13*)	117.94	117.72 (*13*)
ethyl acetate	0.8943	0.8946 (*13*)	77.10	77.15 (*13*)
vinyl acetate	0.9255	0.9321^a (*10*)	72.86	72.6 (*10*)

^{a} At 20 °C.

Experimental Section

The authors (*7*) previously proposed the flow-type apparatus for measuring isobaric dew and bubble points. In the present modification, the dew point still and the bubble point still are reversed in order to reduce the time required for the experiment. The construction of the feeder is further modified to keep the constant flow rate. The modified experimental apparatus is schematically shown in Figure 1. The apparatus is entirely made of borosilicate glass. Its main parts are a bubble point still, B, a dew point still, D, three overflow tubes, O, and a feeder, F. The internal construction of both stills is almost similar to that of the small ebulliometer (*4*, *7*). An electric cartridge heater is inserted into each boiling flask, and a little glass dust is put on the wall of the heat-transfer surface to stabilize the boiling condition. In each still, the boiling vapor–liquid mixture rises through a Cottrell tube and flashes to a thermometer well. The amount of liquid contained in each still is about 15 cm^3; both stills are kept adiabatic with evacuated jackets and tapes. As shown in Figure 1, feeder F is modifid to keep the liquid level constant in it. The experimental temperatures were measured with the Hewlett-Packard 2804A quartz thermometers, calibrated by the triple point of water in a reference cell. The reliability of the thermometers used seems ±0.01 °C. The atmospheric pressures were indirectly measured by the bubble points of water in a separate ebulliometer.

Special grade reagents were supplied by the Wako Chemicals Co., Ltd. Ethyl acetate was purified with distillation. Acetic acid and vinyl acetate were used without further purification.

0021-9568/88/1733-0499$01.50/0