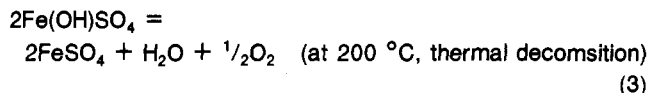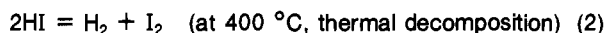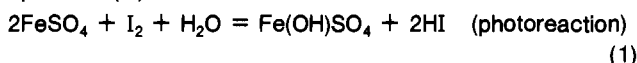# Viscosities of Aqueous Hydrochloric Acid Solutions, and Densities and Viscosities of Aqueous Hydroiodic Acid Solutions

E. Nishikata,[†] T. Ishii,* and T. Ohta[‡]

Departments of Chemical and Electrical Engineering, Yokohama National University, Yokohama, Japan 240

The viscosities of aqueous hydrochloric acid solutions were measured in the concentration range 0–36 wt % at temperatures of 10–40 °C. The densities and viscosities of aqueous hydroiodic acid solutions were measured in the concentration range 0–57 wt % at temperatures of 10–40 °C.

There are many recycle processes of H_2O decomposition in the hydrogen energy problem. In these processes H_2O is decomposed into HCl or HI. For example, in the Yokohama mark 6 process (7):

$$2FeSO_4 + I_2 + H_2O = Fe(OH)SO_4 + 2HI \quad \text{(photoreaction)} \tag{1}$$

$$2HI = H_2 + I_2 \quad \text{(at 400 °C, thermal decomposition)} \tag{2}$$

$$2Fe(OH)SO_4 =$$
$$2FeSO_4 + H_2O + {}^1/_2O_2 \quad \text{(at 200 °C, thermal decomsition)} \tag{3}$$

where the gas mixture of HI, H_2, and I_2 formed in reaction 2 is quenched, and I_2 is solidified and separated, as the I_2 vapor pressure is very small at room temperature.

Next, the gas mixture of HI and H_2 is absorbed into water, and HI and H_2 are separated into aqueous HI solution and H_2 gas (3), as HI gas is an acid gas and has a large solubility, and H_2 gas has a very small solubility. The aqueous HI solution is separated into HI gas and H_2O by distillation.

Therefore, measurements of the properties of aqueous HCl and HI solutions are of great importance in the hydrogen energy problem.

Thus, the viscosities of aqueous HCl solutions and the densities and viscosities of aqueous HI solutions are measured in this study. High-purity aqueous 36 wt % HCl and 57 wt % HI solutions were obtained from Kokusan Chemicals, Ltd.

Experimental Section and Discussions

Viscosities of Aqueous HCl Solutions. The kinematic viscosities of aqueous HCl solutions were measured by using Cannon–Fenske viscometers in a thermostated bath. The measured kinematic viscosities of aqueous HCl solutions are tabulated in Table I. The accuracy of the kinematic viscosities was within ±99.85%. The viscosities of the aqueous HCl solutions were calculated from the measured kinematic viscosities. The densities of the aqueous HCl solutions were interpolated from the data of I.C.T. (1). The concentrations of aqueous HCl solutions were determined by titration of 0.1, 0.5, and 1 N aqueous NaOH solution, and were about 5, 7.5, 10, 12.5, 15, 17.5, 20, 22.5, 25, 27.5, 30, 33, and 36 wt % at temperatures of 10, 15, 20, 25, 30, 35, and 40 °C. The accuracy of the temperature measurement was ±0.01 °C except for that at 10 °C which was ±0.1 °C.

In the calculation of the normality as weight percent, the densities of aqueous HCl solutions were needed and were already measured over wide concentration and temperature ranges (1). However, in the previous study reliable viscosities of aqueous HCl solutions were measured at only 20 and 25 °C

Table I. Kinematic Viscosities (cSt) of Aqueous HCl Solutions

wt %	temp, °C						
	10.00	15.00	20.00	25.00	30.00	35.00	40.00
4.17	1.3432	1.2008	1.0058	0.9541	0.8612	0.7794	0.7239
8.11	1.3803	1.2255	1.1019	0.9912	0.8979	0.8002	0.7435
10.02	1.3917	1.2530	1.1127	1.0061	0.9218	0.8334	0.7738
12.44	1.4030	1.2614	1.1433	1.0310	0.9458	0.8509	0.7875
14.57	1.4386	1.2876	1.1670	1.0635	0.9669	0.8775	0.8281
17.37	1.4732	1.3297	1.2086	1.0975	1.0046	0.9128	0.8532
18.66	1.4936	1.3490	1.2377	1.1252	1.0347	0.9342	0.8841
21.92	1.5517	1.4106	1.2898	1.1797	1.0789	0.9895	0.9250
24.93	1.6071	1.4682	1.3483	1.2332	1.1368	1.0352	0.9760
27.05	1.6603	1.5072	1.3873	1.2757	1.1675	1.0722	1.0058
29.0	1.7263	1.5841	1.4462	1.3183	1.2209	1.1209	1.0591
32.2	1.8638	1.7002	1.5603	1.3730	1.3208	1.2227	1.1371
36.0	2.0446	1.8693	1.7224	1.5667	1.4346	1.3250	1.2445

Table II. Viscosities (cP) of Aqueous HCl Solutions

wt %	temp, °C						
	10.00	15.00	20.00	25.00	30.00	35.00	40.00
4.17	1.3715	1.2237	1.1054	0.9694	0.8742	0.7904	0.7326
8.11	1.4397	1.2733	1.1427	1.0269	0.9285	0.8259	0.7666
10.02	1.4627	1.3145	1.1650	1.0524	0.9624	0.8693	0.8056
12.44	1.5021	1.3384	1.2119	1.0908	0.9988	0.8977	0.8293
14.57	1.5451	1.3816	1.2487	1.1369	1.0308	0.9337	0.8795
17.37	1.6014	1.4428	1.3090	1.1854	1.0830	0.9822	0.9164
18.66	1.6356	1.4745	1.3504	1.2243	1.1237	1.0127	0.9567
21.92	1.7271	1.5672	1.4291	1.3048	1.1901	1.0895	1.0166
24.93	1.8145	1.6533	1.5156	1.3825	1.2710	1.1553	1.0863
27.05	1.8928	1.7137	1.5733	1.4442	1.3182	1.2073	1.1296
29.0	1.9853	1.8186	1.6560	1.5055	1.3907	1.2734	1.1990
32.2	2.1712	1.9757	1.8085	1.5873	1.5229	1.4074	1.3054
36.0	2.4229	2.2096	2.0308	1.8425	1.6871	1.5503	1.4524

(2), and curiously we have no data over wide concentration and temperature ranges yet. The data of I.C.T. (2) at only 25 °C are slightly larger than our data at high concentrations and already out of date. The data from the CRC Handbook (4) at only 20 °C agree with our data. The few data of Kagaku-Benran (5) at 0, 10, and 20 °C agree with our data.

In this study the viscosities were measured three times for each run, and the average value was calculated and tabulated in Table II and shown in Figure 1.

Densities of Aqueous HI Solutions. The densities of aqueous HI solutions have not been measured yet. The densities of the solutions were determined with standard small-scale picnometers in a thermostated bath. The volume of the picnometer was about 5.0 cm³ and accurately measured by filling the picnometer with distilled water, keeping the picnometer in the thermostat bath for a long time, weighing the distilled water in the picnometer, and interpolating the density of pure water (6) at each temperature for each run. The accuracy of the measured densities was within ±99.85%. This procedure is conventional. The concentrations of the solutions were determined by titration of 0.1, 0.5, and 1 N aqueous NaOH solutions, and were about 5, 10, 15, 20, 25, 30, 40, 45, 50, and 55 wt % at 10, 15, 20, 25, 30, 35, and 40 °C. The accuracy of the temperatures was ±0.01 °C except for that at 10 °C which was ±0.1 °C. In the calculation of the normality as weight percent the measured densities of the solution were used. The measurements of the densities of the solutions were
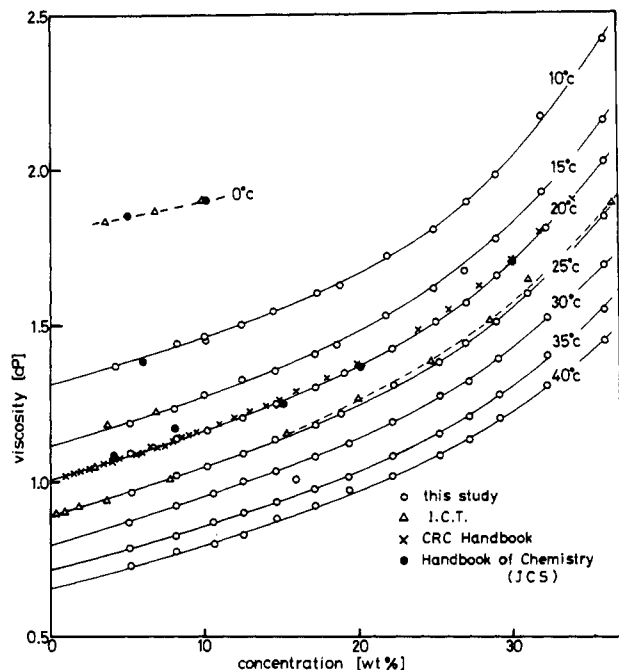
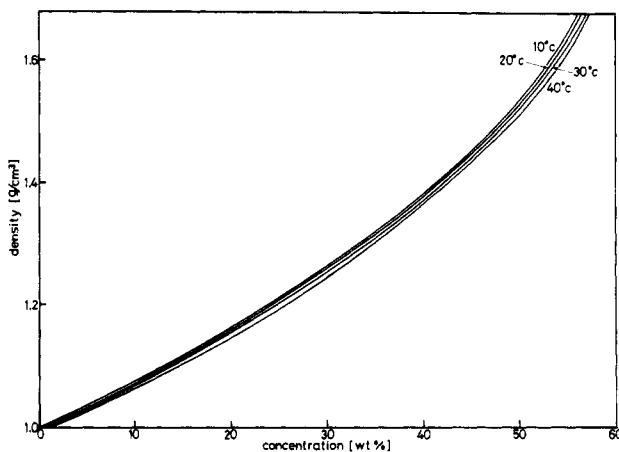**Figure 1.** Viscosities of aqueous hydrochloric acid solutions.

Figure 2. Densities of aqueous hydroiodic acid solutions.

Table III. Densities (g/cm³) of Aqueous HI Solutions

	temp, °C						
wt %	10.00	15.00	20.00	25.00	30.00	35.00	40.00
5.2	1.0362	1.0349	1.0342	1.0324	1.0304	1.0287	1.0275
10.8	1.0835	1.0826	1.0812	1.0802	1.0787	1.0768	1.0745
16.4	1.1296	1.1280	1.1226	1.1245	1.1220	1.1195	1.1164
22.4	1.1810	1.1780	1.1765	1.1753	1.1740	1.1717	1.1692
27.2	1.2360	1.2348	1.2333	1.2319	1.2303	1.2270	1.2235
33.1	1.2955	1.2934	1.2918	1.2900	1.2878	1.2864	1.2820
38.7	1.3651	1.3628	1.3604	1.3565	1.3529	1.3490	1.3455
42.9	1.4276	1.4245	1.4208	1.4176	1.4139	1.4100	1.4060
48.7	1.5134	1.5108	1.5072	1.5036	1.4996	1.4956	1.4908
53.0	1.5976	1.5945	1.5913	1.5875	1.5834	1.5786	1.5734
57.0	1.7002	1.6968	1.6933	1.6885	1.6855	1.6809	1.6960

done three times for each run and showed negligible scatter.

The average densities are tabulated in Table III and shown in Figure 2.

Viscosities of Aqueous HI Solutions. The viscosities of aqueous HI solutions have not been measured yet. The kinematic viscosities of the same solutions as used in the measurements of the densities were determined with Cannon–Fenske viscometers in the thermostated baths which were used in the previous measurements of the kinematic viscosities of aqueous HCl solutions. The measured kinematic viscosities of

Table IV. Kinematic Viscosities (cSt) of Aqueous HI Solutions

	temp, °C						
wt %	10.00	15.00	20.00	25.00	30.00	35.00	40.00
5.2	1.2478	1.0931	0.9699	0.8641	0.7795	0.7015	0.6387
10.8	1.1952	1.0426	0.9285	0.8358	0.7485	0.6799	0.6230
16.4	1.1212	0.9895	0.8793	0.7965	0.7220	0.6571	0.6001
22.4	1.0686	0.9433	0.8497	0.7704	0.6952	0.6353	0.5826
27.2	0.9991	0.8970	0.8117	0.7356	0.6686	0.6145	0.5665
33.1	0.9519	0.8633	0.7814	0.7162	0.6572	0.6019	0.5578
38.7	0.9176	0.8318	0.7630	0.7116	0.6368	0.5903	0.5473
42.9	0.9042	0.8208	0.7524	0.6925	0.6349	0.5885	0.5470
48.7	0.8904	0.8136	0.7458	0.6899	0.6343	0.5905	0.5509
53.0	0.9004	0.8259	0.7592	0.7025	0.6461	0.6044	0.5645
57.0	0.9335	0.8657	0.7973	0.8218	0.6857	0.6420	0.5931

Table V. Viscosities (cP) of Aqueous HI Solutions

|	temp, °C						
wt %	10.00	15.00	20.00	25.00	30.00	35.00	40.00
5.2	1.2930	1.1313	1.0031	0.8921	0.8032	0.7217	0.6563
10.8	1.2951	1.1288	1.0039	0.9029	0.8075	0.7322	0.6695
16.4	1.2666	1.1162	0.9907	0.8957	0.8101	0.7358	0.6700
22.4	1.2621	1.1113	0.9997	0.9055	0.8162	0.7444	0.6812
27.2	1.2349	1.1077	1.0011	0.9062	0.8226	0.7540	0.6932
33.1	1.2333	1.1167	1.0095	0.9239	0.8400	0.7743	0.7151
38.7	1.2527	1.1336	1.0381	0.9653	0.8616	0.7964	0.7365
42.9	1.2909	1.1693	1.0691	0.9817	0.8978	0.8299	0.7692
48.7	1.3476	1.2293	1.1241	1.0374	0.9512	0.8833	0.8213
53.0	1.4386	1.3170	1.2082	1.1153	1.0231	0.9542	0.8882
57.0	1.5873	1.4690	1.3501	1.3877	1.1558	1.0792	1.0059
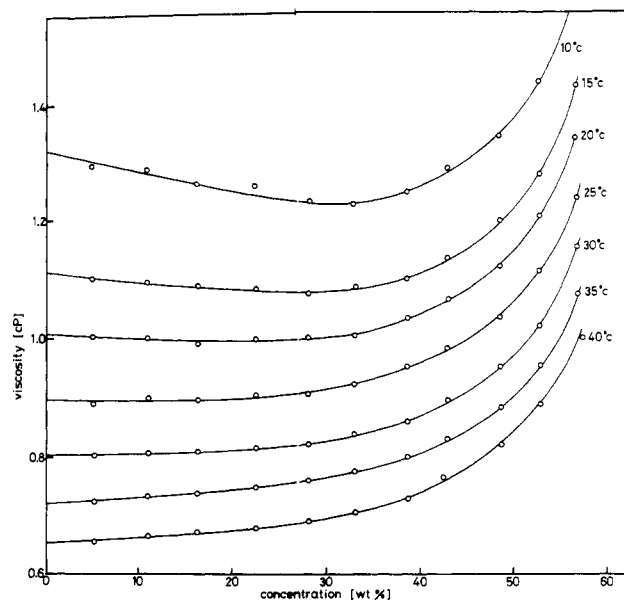
Figure 3. Viscosities of aqueous hydroiodic acid solutions.

aqueous HI solutions were tabulated in Table IV. The accuracy of the measured kinematic viscosities of aqueous HI solutions was within ±99.85%. The viscosities of the aqueous HI solutions were calculated from the measured kinematic viscosities. The densities of the aqueous HI solutions were interpolated from the measured data of the previous section. The range of concentration and temperature is the same as for the measurement of the densities. The viscosities were measured three times for each run, and the average viscosities are tabulated in Table V and shown in Figure 3.

At low temperatures we have minimum viscosity points as shown in Figure 3, which do not exist in the viscosities of aqueous HCl solution, although the densities of both solutions increase monotonously with increase in concentration. The minimum viscosity points at 10, 15, and 20 °C are 33.0, 28.7, and 16.4 wt %, respectively.

As iodine compounds have a peculiar behavior, aqueous HI solutions may be ordered near the minimum density points.

In hydrogen energy recycle processes it is convenient to flow aqueous HI solutions of minimum viscosities in pipes, as the pressure drop of the solution through the pipes is minimum.

Literature Cited

(1) I.C.T. **1928**, *3*, 54, 104.
(2) I.C.T. **1928**, *5*, 12.
(3) Notoji, T., Bachelor Thesis, Department of Chemical Engineering, Yokohama National University, 1977.
(4) Weast, R. C.; Selby, S. M. "CRC Handbook of Chemistry and Physics"; CRC Press: Cleveland, 1974; 54th ed, p D-231.
(5) Japanese Chemical Society; "Kagaku-Benran Fundamentals-2"; Maruzen, 1975; p 580.
(6) Perry, R. H.; Chilton, C. H., "Chemical Engineers' Handbook"; McGraw-Hill: New York, 1973; 5th ed, p 3-71.
(7) Ohta, T. "Solar-Hydrogen Energy Systems"; Pergamon Press: New York, 1979; p 120.

Three-Phase Liquid–Liquid–Vapor Equilibria Behavior of Certain Binary CO₂-n-Paraffin Systems

John D. Hottovy, Kraemer D. Luks, and James P. Kohn*

Department of Chemical Engineering, University of Notre Dame, Notre Dame, Indiana 46556

The three-phase liquid–liquid–vapor loci of four binary CO₂-n-paraffin systems (n-dodecane, n-tridecane, n-tetradecane, n-pentadecane) are studied, and temperature, pressure, and molar volumes and compositions of both liquid phases are reported. It is within this group of n-paraffins that the nature of the upper critical end point for the CO₂-containing binary systems changes from a UCST (L—L-V) to a K point (L–L—V) with increasing carbon number. These four loci are compared with earlier obtained loci on CO₂-n-decane and CO₂-n-eicosane.

Introduction

There is an increasing interest in CO₂-hydrocarbon phase equilibria data relevant to the process of using CO₂ injection for enhanced oil recovery. Such data are useful for determining interaction parameters in equations of state purporting to be applicable to describing the phase equilibria in such multicomponent systems. These equations of state would be used to describe three-phase L₁-L₂-V phase equilibria as well as two-phase L-V and L₁-L₂ phase equilibria (*1*).

Schneider (*2*) has reported that the binary L₁-L₂-V loci of the CO₂-n-paraffin systems undergo a transition in phase behavior as one increases the carbon number. Specifically, the CO₂-n-tridecane locus terminates at the upper end (higher P and T end) with a UCST (L₁—L₂-V) while the CO₂-n-hexadecane locus terminates with a K point (L₁-L₂—V). This observation is consistent with our detailed studies of the binary systems CO₂-n-decane (*3*) and CO₂-n-eicosane (*4*), the former exhibiting a UCST and the latter a K point as the upper termination point to its L₁-L₂-V locus.

In this paper, we present detailed studies of the L₁-L₂-V loci of the binary systems CO₂ with n-dodecane, n-tridecane, n-tetradecane, and n-pentadecane, respectively. Knowledge of these systems in the vicinity of the above-mentioned transformation in L₁-L₂-V loci will be useful to testing correlations and obtaining interaction parameters for L₁-L₂-V phase equilibria calculations. In particular, a strong case could be made for a correlation which not only predicts L₁-L₂-V phase equilibria for these binary systems but also correctly signals the change in L₁-L₂-V loci with increasing carbon number at the correct place, namely (as will be shown), between the systems CO₂-

n-tridecane and CO₂-n-tetradecane.

Experimental Section

A detailed description of the experimental equipment and procedure is given elsewhere (*4*, *5*). Briefly, a known amount of n-paraffin was placed in a 10-mL glass equilibrium cell. During experimental runs, measured amounts of CO₂ gas were added to the thermostated equilibrium cell from a high-pressure bomb, through the use of a positive displacement mercury pump. By a mass balance the moles of CO₂ in a liquid phase can be determined (the vapor phase is assumed to be pure CO₂ due to the low volatility of these paraffins at the temperatures of interest). In studying a L₁-L₂-V system, the moles of CO₂ in an *individual* liquid phase were determined by making a run in which the *other* liquid phase was present in a trace (but visible) amount. Thus two runs were required to obtain the properties of both L₁ and L₂. Procedures for determining the termination points of the L₁-L₂-V loci (see Table V) are routine and are detailed elsewhere (*4*).

Temperature was measured with a Pt-resistance thermometer to an estimated accuracy of ±0.02 K for the L₁-L₂-V data. Pressure was measured with Bourdon tube gauges, which were frequently calibrated against an accurate dead-weight gauge, to an estimated accuracy of ±0.07 bar. The viewable glass equilibrium cell was volumetrically marked and calibrated and gave volumetric readings to an accuracy of ±0.02 mL.

Materials

The n-paraffins were purchased from the Humphrey-Wilkinson Co. at a stated purity of 99%. Melting point depression determinations indicated impurity levels of 0.47% (n-dodecane), 2.02% (n-tridecane), 1.12% (n-tetradecane), and 0.34% (n-pentadecane) based on literature values (*6*) of the melting points. The n-paraffins were used without further purification.

The CO₂ (mol wt = 44.01) used in this study was obtained from the Matheson Co. as "Coleman Grade" material with a stated minimum purity of 99.99%. Oxygen, nitrogen, carbon monoxide, and hydrogen were the major impurities.

The CO₂ was prepared for use by flashing it from the cylinder at room temperature to the 2000-cm³ storage reservoir maintained at 0 °C. When this is done, the resulting liquefaction of the CO₂ makes it free from impurities, the impurities remaining