SOLUBILITIES OF GASES IN AQUEOUS SOLUTIONS OF WEAK ACIDS*

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Solubility data of gases in aqueous solutions are very important to engineers in practical uses such as gas-liquid contact operation. Hence, many experimental data have been reported for various gas solubility systems in aqueous solutions. For the solubilities of gases in aqueous electrolyte solutions in particular there are plentiful data, and also some empirical correlations have been presented by Markham and Kobe^{1,2)}, van Krevelen and Hoftijzer⁷⁾, and Onda *et al.*^{3,4)}. For other gas-aqueous solution systems, however, few experimental data have been presented and no quantitative correlation has yet been proposed.

For aqueous solutions of weak electrolytes such as the organic acids and amines, it should be emphasized that there are no experimental data. Considering these, the authors have recently observed the solubilities of nitrous oxide and ethylene in aqueous solutions of monoethanolamine and discussed the possibility of prediction⁶⁾.

In the present work, in order to build up gas solubility data for these systems, solubilities of carbon dioxide and nitrous oxide in aqueous solutions of the weak acids were measured by a volumetric method at 1 atm and 25°C, and the results studied.

Experimental

Experimental apparatus and procedures adopted in this work were the same as those in the previous papers^{3,4,6)}. As shown in that work, the reliabilities of the apparatus and procedures have been confirmed.

Reagent grade weak acids of guaranteed purity were used without further purification, and distilled water was used. In **Table 1**, the densities and refractive indices of water, formic acid, acetic acid and propionic acid at 25°C are shown to compare with the values in the literature⁵⁾. For gases, on the other hand, carbon dioxide was supplied from a commercial cylinder, and nitrous oxide of high purity was supplied by Showa Denko Co., Ltd., in Tokyo, and the purities were verified by gas chromatographic analyses as more than 99.8% for both.

The concentration of weak acid was determined by volumetric titration with sodium hydroxide to a phenolphthalein end-point.

Solubilities of carbon dioxide and nitrous oxide in pure water at 25°C were 0.7597 and 0.5512, respectively, as the Bunsen absorption coefficients. The accuracy of these values has been discussed elsewhere^{3,6)}.

The systems studied in this work are as follows: carbon dioxide-formic acid, acetic acid, propionic acid, oxalic acid, citric acid and phosphoric acid, and nitrous oxide-formic acid, acetic acid, propionic acid and oxalic acid.

Results and Discussion

The results of the solubility determinations are shown in **Table 2** for carbon dioxide and in **Table 3** for nitrous oxide. These results are also shown in graphical form in **Figs. 1, 2 and 3**. In these figures, the dependence of $\log(\alpha/\alpha_w)$, which means the negative logarithm of the activity coefficient of the gas species, on the concentration of weak acid is represented. As can be seen from these figures, these plots cannot be correlated by straight lines as in the case of aqueous salt solutions. Furthermore, these curves are all concave in contrast to those for the aqueous solutions of monoethanolamine.

In general, solubility of gas is discussed based on the thermodynamic behavior of the solution. However, for aqueous solution of weak acid, this seems to be very complicated since the molecules of the weak acid dissociate partially into ions in the aqueous solution, and the fraction of dissociated species cannot be neglected in some cases. Therefore, in the present work, an empirical correlation of solubility data was attempted.

As previously mentioned, the Setchenow equation is not applicable to such cases, so the authors tried to correlate the experimental results by the following hyperbolic equation.

$$\frac{\alpha}{\alpha_w} = aC + \frac{1}{1 + bC} \quad (1)$$

This equation was proposed by Markham and Kobe^{1,2)}

Table 1 Physical properties of water and organic acids

Substance	d^{25}		n_D^{25}	
	obs.	lit. ⁵⁾	obs.	lit. ⁵⁾
Water	—	0.99704	1.3325	1.3325
Formic acid	1.1998	1.21405	1.3688	1.36938
Acetic acid	1.0440	1.04366	1.3718	1.3698
Propionic acid	0.9883	0.9880	1.3845	1.3843

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Fig. 1 Solubilities of carbon dioxide in aqueous solutions of weak acids at 1 atm and 25°C (1)

Fig. 2 Solubilities of carbon dioxide in aqueous solutions of weak acids at 1 atm and 25°C (2)

Fig. 3 Solubilities of nitrous oxide in aqueous solutions of weak acids at 1 atm and 25°C

Table 2 Solubilities of carbon dioxide in aqueous weak acid solutions at 1 atm and 25°C

Weak acid	C	α
Formic acid	0.3607	0.7480
	0.7014	0.7422
	1.2525	0.7432
	1.4028	0.7472
	2.7204	0.7632
	3.5120	0.7790
Acetic acid	0.4282	0.7667
	0.9155	0.7712
	1.7973	0.7887
	2.5150	0.8108
	2.7928	0.8212
	3.7938	0.8561
	3.8939	0.8591
	4.2993	0.8844
Propionic acid	0.5405	0.7655
	1.1414	0.7769
	1.9819	0.7924
	2.5727	0.8164
	2.6379	0.8140
	3.0330	0.8358
	4.0922	0.9127
Oxalic acid	4.7848	0.9971
	0.1774	0.7512
	0.3861	0.7447
	0.5110	0.7418
	0.7776	0.7357
Citric acid	0.9013	0.7374
	0.1867	0.7381
	0.3874	0.7179
	0.7365	0.6966
	1.0477	0.6741
	1.2662	0.6648
	1.3524	0.6611
Phosphoric acid	0.7013	0.6714
	1.0923	0.6405
	1.6024	0.6076
	1.7412	0.5958
	2.0573	0.5731

Table 3 Solubilities of nitrous oxide in aqueous weak acid solutions at 1 atm and 25°C

Weak acid	C	α
Formic acid	0.6234	0.5481
	1.3125	0.5529
	1.4033	0.5542
	2.4451	0.5579
	2.8999	0.5653
Acetic acid	0.3096	0.5476
	0.5012	0.5472
	0.5466	0.5458
	0.6188	0.5472
	1.1204	0.5610
	1.8731	0.5742
	2.2123	0.5814
	2.2750	0.5815
	2.6174	0.5897
	2.6975	0.5899
Propionic acid	3.2019	0.6071
	3.5392	0.6193
	3.7865	0.6227
	0.4319	0.5583
	0.8473	0.5612
	1.3523	0.5711
Oxalic acid	2.3654	0.5985
	3.2994	0.6481
	0.2091	0.5471
	0.2433	0.5468
	0.5227	0.5418
	0.8434	0.5380
	0.8567	0.5353

Table 4 Values of a and b

Gas	Weak acid	a	b
CO ₂	Formic acid	0.1018	0.1399
	Acetic acid	0.1066	0.0997
	Propionic acid	-0.0838	-0.0867
	Oxalic acid	0.1460	0.2147
	Citric acid	0.0861	0.2412
	Phosphoric acid	0.0382	0.2280
N ₂ O	Formic acid	0.0716	0.0776
	Acetic acid	0.1231	0.1298
	Propionic acid	0.1529	0.1523
	Oxalic acid	0.0335	0.0683

to correlate the solubilities of carbon dioxide and nitrous oxide in aqueous salt solutions. In this work, however, the Bunsen absorption coefficient and molar-

ty are used as solubility and concentration of solute, respectively. The experimental results were fitted to this equation by the nonlinear least square method. The calculated values of a and b are listed in **Table 4**, and the fitting curves of Eq.(1) to the experimental data are also shown in Figs. 1, 2 and 3. From these figures, it is found that Eq.(1) can correlate the solubility data for these systems well. The standard deviation of this correlation was 0.0140.

Nomenclature

a	= constant in Eq.(1)	[l/mole]
b	= constant in Eq.(1)	[l/mole]
C	= molarity of weak acid	[mole/l]
d^{25}	= density at 25°C	[g/cm ³]

n_D^{25}	= refractive index at 25°C	[—]
α	= Bunsen absorption coefficient	[—]

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REMARKS ON THERMODYNAMIC CONSISTENCY TESTS OF MULTICOMPONENT VAPOR-LIQUID EQUILIBRIUM DATA*

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Introduction

Thermodynamic consistency tests of ternary isothermal vapor-liquid equilibrium data based upon the direct use of the Gibbs-Duhem equation have been proposed in the literature^{9,12,13}. Herington⁹) suggested that graphical integration should be performed either on lines of constant mole ratio of two components, or on lines of constant mole fraction of one of the components. The method usually requires that experimental data must lie on the selected lines. Since experimental data are not generally observed on the selected lines, the interpolation of existing data is unavoidable to provide values on the chosen lines. The necessity of a great number of experimental data and that of interpolation may be the major disadvantages of the method. To avoid these disadvantages, Li and Lu¹²) proposed a method that involves numerical integration around selected loops of experimental points. The method is called the closed or the open test, depending upon whether the first and last points in the loops may or may not be linked. Li and Lu placed on their test only the limitation that the points should not be widely separated so that the error in numerical integration will be minimized. McDermott and Ellis¹³) stated that the open loop only tests the end points and does not test the internal points in the loop, and that the open and closed loop tests on the same points can give different deviations when random errors are present. They modified the Li-Lu test to present a pair consistency test. Such consistency tests

may be possible by use of some analytical functions expressing the liquid-phase activity coefficient as a function of composition and temperature. Considerable amounts of effort have been made to show the applicability of these equations in the calculation of multicomponent vapor-liquid equilibrium data. The local composition equations which have built-in temperature terms can predict multicomponent equilibrium data from only binary parameters without any additional parameter with better accuracy than the Margules and van Laar equations do²⁰). The present author¹⁷) did extensive studies concerning the prediction accuracy of the Wilson, nonrandom two-liquid (NRTL), and Heil equations for seventy eight multicomponent systems and demonstrated that the Wilson equation is the best in overall performance on the basis of the systems studied.

In this work the author will show that the Li-Lu and McDermott-Ellis tests and the Redlich-Kister equation cannot always check experimental errors of particular forms which the Wilson equation may predict.

Basic Equations

The condition for consistency described by Li and Lu is

$$\sum_{n=1}^N \sum_{i=1}^M x_{i(n)} [\ln \gamma_{i(n-1)} - \ln \gamma_{i(n+1)}] = 0 \quad (1)$$

where n refers to the n -th point in the loop of N points. M is the number of components.

McDermott and Ellis suggested the pair consistency equation

$$D = \sum_{i=1}^M [x_{i(n)} + x_{i(n+1)}] [\ln \gamma_{i(n+1)} - \ln \gamma_{i(n)}] \quad (2)$$

where the absolute value of D lies between 0.00 and

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