



SOLUBILITY OF SOME NON-POLAR GASES IN MIXED SOLVENTS

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ABSTRACT

The scale particle theory predicting has solubilities in mixed solvents at 1 atmosphere pressure and ordinary temperature has been studied. A method for predicting Henry's law constant of single gas in mixed solvents, from the corresponding data of pure components by using statistical mechanical theory is presented. Good agreement with experimental results are obtained for helium, argon, nitrogen, oxygen, methane and ethylene gases in a variety of solvent mixture (water, methanol, ethanol, 1-propanol, 2-propanol, 1,2-diethanediol, acetone, n-hexane and n-dodecane).

Key words: Solubility, Scale particle theory, Henry's law, Mixed solvent.

INTRODUCTION

Guha and Panda¹⁻⁴ reported the solubility of single solute gas including freons in liquid such as water, carbon tetrachloride, benzene and its derivatives and benzene-hydrocarbon vapor mixture in water. In this paper, the study of solubility of non-polar gases in mixed solvent has been presented.

While the solubility of single gas in mixed solvents is of industrial importance, most experimental works have dealt with solubilities in single solvent. For mixed solvents, therefore, prediction schemes are often used. In the part of several years, a considerable efforts has been devoted to the problem of predicting the solubility of gases in mixed solvents. A large number of experimental and theoretical works have been done on solubility of dingle gas in single solvent but relatively experimental as well as theoretical investigations of solubility of gases in mixed solvents are rare.

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Tiepel and Gubbins⁵ have proposed an analysis by statistical mechanical perturbation theory. The perturbation techniques have used to predict mixed solvent Henry's law constants for the pure solutes. This method appears promising, especially when liquid-vapor equilibrium data for mixed solvent are not available. The calculations required are formidable, however, and the accuracies of perturbation methods have not been fully established. Gibbins⁶ has given a review of the subject.

O'Connell and Prausnit⁷, and Boublik⁸ have analyzed the phenomena of solubility in mixed solvent from purely thermodynamics viewpoints and derived semi-theoretical correlations. O'Connell⁹ briefly reviewed the concept of these theoretical treatments. The general thermodynamic relation between Henry's law constant for a solute in a mixed solvent is discussed in terms of limiting activity coefficients. It has also pointed out the limitation of the thermodynamic treatments and proposed an approximate correlation based on the solution theory of Kirkwood and Buff¹⁰. Several unknown integrals in the theory are approximated by an empirical function of solvent composition and of solvent properties which generally predicts experimental data for gases in both; simple and complex solvents.

Puri and Ruther¹¹ proposed an additive excess free energy model for predicting Henry's law constant in mixed solvents. They utilized solvent-vapor liquid equilibrium data and new model based on the Van Laar equation.

Kung *et al.*¹² developed a method for prediction of Henry's law constants of single gases in mixed solvents from the corresponding binary data and by using one parameter from the Wilson¹³ equation is presented. The average absolute error for 40 such binary solvent systems is 5.9%. For a system containing water in which gas solubilities are typically low, the proposed method and the other ones-give unreliable results.

Catte *et al.*¹⁴ proposed a new and simple model based on group contribution method for predicting gas solubilities in mixed solvents at low pressure and temperature. The overall performance of this method is better than that a MHV2, GC-EOS and Sander's model but some adjustable parameters are used. However, the applicable range and accuracy of correlation are still not satisfactory. All of these correlation required thermodynamic data for mixed solvents.

A statistical mechanical approach can be thought to be a powerful means for analyzing gas solubility phenomena in mixed solvents. However, at the present time, there is no exact statistical mechanical solution theory. Instead, various kinds of approximate theories or model approaches have been presented.

In the present work, a somewhat intuitive statistical mechanical gas solubility theory has been presented for the cases concerned with pure liquid including water, discussed by Guha and Panda¹⁻⁴ in the previous papers, has been extended to the system of mixed solvents.

Method of computation

Solubility and thermodynamic functions solutions pertaining to the solution process are calculated in usual manner utilizing scale particle theory (SPT) formalism, considering that dissolution of gas in a liquid takes place through two steps:

- (i) First, the creation of a cavity in the solvent of suitable size to accommodate the solute molecules i.e. its diameter is exactly the hard sphere diameter of the solute gas. This referred to as a cavity formation process. The free energy associated with this process is called cavity formation energy (CFE).
- (ii) The second step involved introduction of solute molecule into the cavity of the solvent and hence, interaction between solute and solvent occurs according to some potential law. The energy associated with this process is called Gibbs free energy of interaction.

the solubility of gas in liquid is described by Henry's law constant as –

$$\lim_{x_2 \rightarrow 0} \left(\frac{f_2}{x_2} \right) = K_H \quad \dots(1)$$

for extremely dilute solution, from statistical mechanics, Henry's law constant can be written as¹⁵⁻¹⁷.

$$RT \ln K_H = \mu_{\text{cav}} + G_{\text{m},i} + RT \ln(RT/V_{\text{m},1}) \quad \dots(2)$$

for mixed solvent, this can be rewritten as –

$$RT \ln K_{H,\text{mix}} = (\mu_{\text{cav}})_{\text{mix}}(d) + (G_{\text{m},i})_{\text{mix}} + RT \ln \{RT/(V_{\text{m},1})_{\text{mix}}\} \quad \dots(3)$$

Where $(\mu_{\text{cav}})_{\text{mix}}(d)$ is the cavity formation energy to make one mole of cavity in the mixed solvent and each cavity is sufficiently large to hold one gas molecule. $(G_{\text{m},i})_{\text{mix}}$ is the molar Gibb's free energy of interaction between the solute in the cavity and the surrounding molecules of mixed solvents; R is the gas constant; T is the system temperature and $K_{H,\text{mix}}$ is Henry's law constant of gases in mixed solvent and $(V_{\text{m},1})_{\text{mix}}$ is the molar volume of the solvents mixtures.

Cavity formation energy of binary solvent mixtures

The expression of cavity formation energy, discussed in previous papers by Guha and Panda⁴ and Matyushov and Ladanyi,¹⁸ was extended to gas solubility in mixed solvent as –

$$(\mu_{\text{cav}})_{\text{mix}}(d)/RT = -\ln(1-\eta_{\text{mix}}) + 3\eta_{\text{mix}}d/(1-\eta_{\text{mix}}) + 3d^2\eta_{\text{mix}}(2-\eta_{\text{mix}})(1+\eta_{\text{mix}})/2(1-\eta_{\text{mix}})^2 + d^3\eta_{\text{mix}}(1+\eta_{\text{mix}} + \eta_{\text{mix}}^2 - \eta_{\text{mix}}^3)/(1-\eta_{\text{mix}})^3 \quad \dots(4)$$

where $\eta_{\text{mix}} + \pi\rho_{\text{mix}}(\sigma_{1,\text{mix}})^3/6$ is the “compactness factor” of solvent mixture. The number density of mixture is defined by $\rho_{\text{mix}} = N_A/(V_{m,i})_{\text{mix}}$, N_A is Avagadro’s number. The hard sphere diameter of the solvent mixtures, $(\sigma_{1,\text{mix}})$ is calculated by the relation.

$$(\sigma_{1,m})^3 = x_a\sigma_a^3 + x_b\sigma_b^3 \quad \dots(5)$$

where σ_a and σ_b are hard sphere diameters, x_a and x_b are mole fractions of two solvents ‘a’ and ‘b’ in mixture, respectively. The last term of equation (4) is related to the hydrostatic pressure for gas solubility in incompressible liquid mixtures, which can be neglected.

Interaction energy of non-polar solute with mixed solvent

For a non-polar solute gas and polar solvent mixture, the dispersion energy and inductive energy contribute to interaction free energy. If dispersion is approximated by Lennard Jones (6-12) parameters, then the value of $(G_{m,i})_{\text{mix}}$ is given by the following relation –

$$(G_{m,i})_{\text{mix}}/RT = - (32\pi\rho_{\text{mix}}/9kT)[x_a\{(\sigma_a+\sigma_2)/2\}^3 (\epsilon_a\epsilon_2)^{1/2} + x_b\{(\sigma_b+\sigma_2)/2\}^3 (\epsilon_a\epsilon_2)^{1/2}] - 4\pi\rho_{\text{mix}}\mu_{\text{mix}}^2\alpha_2/3kT[x_a\{(\sigma_a+\sigma_2)/2\}^3 + x_b\{(\sigma_b+\sigma_2)/2\}^3] \quad \dots(6)$$

where ϵ_a , ϵ_b and ϵ_2 are Lennard-Jones (6-12) parameters for solvent ‘a’, solvent ‘b’ and solute gas, respectively and μ_{mix} is the dipole moment of the solvent mixture.

Lucas and Feillolay¹⁹ also used similar type of equation in the analysis of enthalpy of some non-polar molecules in aqueous ethanol solutions and salt solutions.

For binary solvent mixture, no experimental values of the dipole moment of solvent ‘a’ (μ_a) and solvent ‘b’ (μ_b) mixtures are available. It is not desirable also to take the linear average of μ_a and μ_b to calculate dipole moment of binary solvent mixture, μ_{mix} as these are vector quantities. The vector addition would depend on the relative special

orientation of the component moment. Moreau and Douheret²⁰ calculated the thermodynamic and physical behavior of water-acetonitrile mixtures experimentally specially the dielectric properties. The relation used for calculation of the dipole moment of the mixture is –

$$\mu(x) = (1-x_b)\mu_a + x_b\mu_b \quad \dots(7)$$

In this equation, μ_a and μ_b are the dipole moments of the pure substances. The major assumption is that the molecules are in random motion and have random orientations. So, the average of the directions are taken into accounts. Therefore, the following relation can be used to calculate dipole moment of solvent mixtures –

$$\mu_{\text{mix}} = x_a\mu_a + x_b\mu_b \quad \dots(8)$$

where μ_a and μ_b are dipole moments of solvent ‘a’ and solvent ‘b’, respectively.

RESULTS AND DISCUSSION

The calculated solubilities in terms of Henry’s law constant of helium in methanol-water, ethanol-water, 1-propanol-water and 2-propanol-water solutions are given in Table 1 and 2. For comparison, experimental solubilities of helium in above solvent mixtures were added in same tables. The correlated results of Henry’s law constant of helium in above mixed solvents are shown in Figs 1-4. Solid lines are for experimental and dashed lines are for calculated results. In these curves, it can be seen that solubilities in mixed solvents increased monotonically with increasing mole fraction of alcohol over the entire composition range except low mole fraction of alcohol ($0 < x_a < 0.2$). The order of gas solubility in the alcohol-water solution was-2-propanol-water > 1-propanol-water > ethanol-water > methanol-water in the full range of composition. Good agreements between experimental and calculated solubilities were found. For above calculations’ necessary molecular parameters are given in Tables 3 and 4. In Table 3, the hard sphere diameter of methanol, ethanol, 1-propanol, and 2-propanol are given at 293.15 K. The hard sphere diameter of alcohols at 298.15K was calculated using the following relation suggested by Wilhelm³³.

$$\sigma_1(T) = \sigma_1^{298.15} + (\delta\sigma_1/\delta T)(T - 298.15 \text{ K}) \quad \dots(9)$$

Here, $\sigma_1^{298.15}$ denotes the effective hard sphere diameter of the solvent at 298.15 K and $\delta\sigma_1/\delta T$ is the temperature coefficient of the hard sphere diameter that is taken from Ben-Amotz and Herschbach³⁴ and Ben-Amotz and Wills²¹.

Table 1. Solubilities in terms of logarithm of Henry's law constant ($\ln K_H/\text{atm}$) of helium gas dissolved in methanol(a) + water(b) and ethanol(a) + water(b) at 298.15 K and 1 atmosphere pressure

Methanol mole fraction (x_a)	Density at 298.15K _H	Expt. $\ln K_H^b/\text{atm}$	Calc. $\ln K_H/\text{atm}$	Ethanol mole fraction (x_a)	Density at 298.15K _H	Expt. $\ln K_H^b/\text{atm}$	Calc. $\ln K_H/\text{atm}$
0.0000	0.9969	11.8463	11.5233	0.0000	0.9969	11.8463	11.5233
0.0351	0.9867	11.7204	11.5108	0.0073	0.9954	11.8438	11.5410
0.0845	0.9748	11.5987	11.4997	0.0373	0.9847	11.7775	11.5537
0.1003	0.9710	11.6099	11.4929	0.1972	0.9334	11.4334	11.3741
0.2620	0.9333	11.4333	11.3423	0.3141	0.9016	11.0703	11.0950
0.5001	0.8814	10.9854	10.9311	0.4156	0.8775	10.8039	10.8746
0.7546	0.8305	10.3380	10.3754	0.4695	0.8659	10.6134	10.6617
0.8729	0.8085	10.1058	10.1053	0.6659	0.8300	10.1288	10.1210
0.9061	0.8025	10.0107	10.0298	0.6748	0.8285	9.8773	10.0977
0.9277	0.7986	9.9789	9.9807	0.9462	0.8043	9.6373	9.6044
1.0000	0.7862	9.7671	9.8206	1.0000	0.7861	9.5243	9.3389

^bYamamoto et al. (ref. 27).

Table 2. Solubilities in terms of logarithm of Henry's law constant ($\ln K_H$ /atm) of helium gas dissolved in 1-propanol(a) + water(b) and 2-propanol(a) + water(b) at 298.15 K and 1 atmosphere pressure.

1-Propanol mole fraction (x_a)	Density at 298.15K _h	Expt. $\ln K_H^b$ /atm	Calc. $\ln K_H$ /atm	1-Propanol mole fraction (x_a)	Density at 298.15K _h	Expt. $\ln K_H^b$ /atm	Calc. $\ln K_H$ /atm
0.0000	0.9969	11.8463	11.5233	0.0000	0.9968	11.8463	11.5233
0.0213	0.9884	11.7574	11.5787	0.0222	0.9857	11.8052	11.5372
0.0387	0.9809	11.7644	11.5941	0.0471	0.9739	11.7288	11.5290
0.0430	0.9790	11.7746	11.5962	0.1140	0.9449	11.5063	11.4162
0.0914	0.9588	11.6035	11.5778	0.1815	0.9193	11.2242	11.2160
0.1304	0.9439	11.4650	11.5174	0.4276	0.8515	10.3290	10.3166
0.1979	0.9208	11.1577	11.3534	0.5336	0.8320	10.1024	9.9648
0.2711	0.8993	10.8787	11.1291	0.5710	0.8266	9.9635	9.8577
0.3194	0.8870	10.7295	10.9704	0.7934	0.8002	9.5731	9.2741
0.4277	0.8639	10.4034	10.6173	0.8416	0.7956	9.4734	9.1618
0.5220	0.8481	10.1944	10.3290	0.9215	0.7881	9.3440	8.9830
0.6623	0.8304	9.7420	9.9500	0.9745	0.7830	9.2692	8.8630
0.7497	0.8216	9.7863	9.7371	1.0000	0.7804	9.2190	8.8052
0.8503	0.8128	9.6216	9.5069				
0.3909	0.8078	9.5463	9.3753				
0.9675	0.8078	9.5463	9.3753				
0.9675	0.8026	9.4581	9.2437				
1.0000	0.7995	9.4196	9.1667				

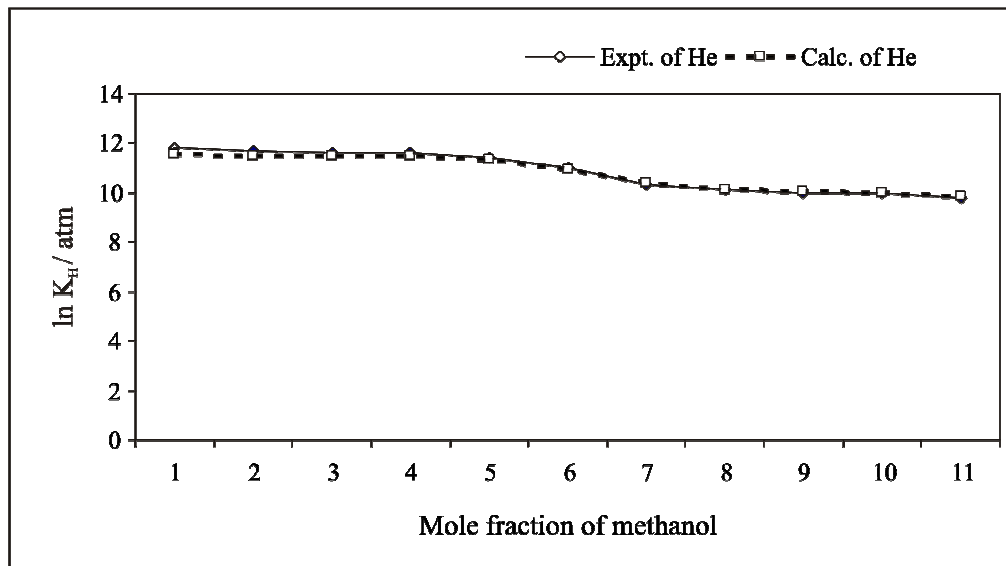


Fig. 1. Solubility of helium in methanol-water solutions as mole fraction of methanol at 298.15 K

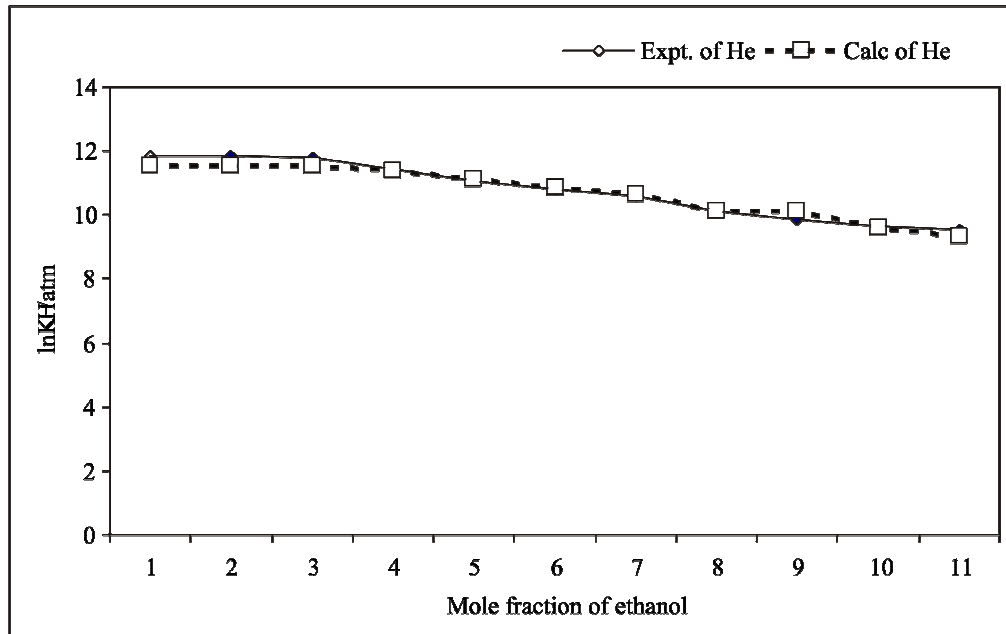


Fig. 2. Solubility of helium in ethanol-water solutions as mole fraction of ethanol at 298.15 K

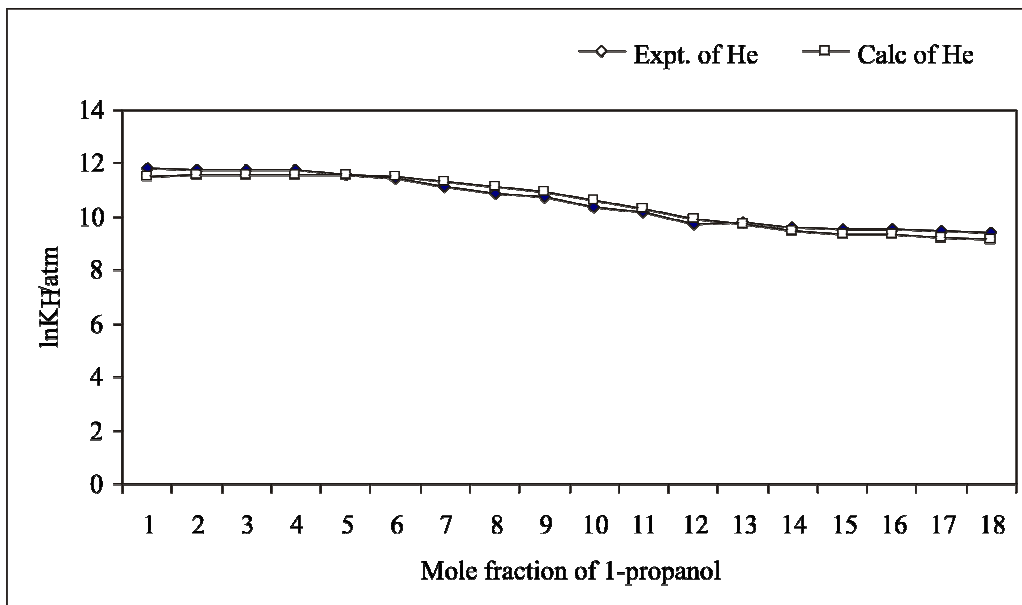


Fig. 3. Solubility of helium in 1-propanol-water solution as a mole fraction of 1-propanol at 298.15 K

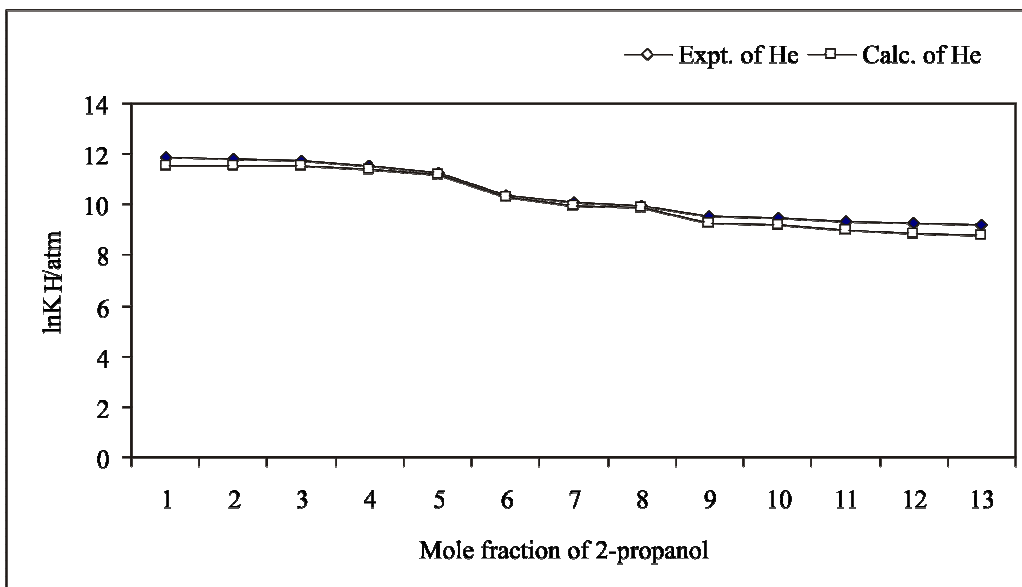


Fig. 4. Solubility of helium in 2-propanol-water solution as a mole fraction of 2-propanol at 298.15 K

Table 3. Selected physical parameters of pure solvents

Solvent	σ/A^0	$(\epsilon/k)/K$	$\mu/(D)^d$	$\alpha/10^{24}(\text{cm}^3\text{mol}^{-1})^d$
Water	2.77 ^a	79.3 ^a	1.84	1.45
Methanol	3.385 ^b	376 ^b	1.70	3.29
Ethanol	4.435 ^b	429 ^b	1.69	5.41
1-Propanol	4.935 ^b	508 ^b	1.68	6.74
2-Propanol	4.895 ^b	460.7 ^b	1.66	7.61
1,2-Ethanediol	4.621 ^b	658 ^b	2.28	5.70
Acetone	4.85 ^b	467 ^b	2.88	6.33
Hexane	5.92 ^c	517 ^c	0.00	13.1
Dodecane	7.85 ^c	715 ^c	0.00	14.45

^aPierotti (ref. 17); ^bBen-Amotz and Wills (ref. 21); ^cWilhelm and Battino (ref. 22); ^dLide (ref. 23).

Table 4. Selected physical parameters of solute gases

Gas	σ/A^0	$(\epsilon/k)/K$	$a/10^{24}(\text{cm}^3\text{mol}^{-1})^d$
He	2.63 ^e	6.03 ^e	0.204
Ar	3.567 ^f	11.70 ^f	1.63
N ₂	3.722 ^e	85.23 ^e	1.74
O ₂	3.541 ^g	88.00 ^g	1.57
CH ₄	3.822 ^e	137.00 ^e	2.70
C ₂ H ₄	4.066 ^e	230.00 ^e	3.70

^eHirschfelder *et al.* (ref. 24); ^fTiepel and Gubbins (ref. 25); ^gTee *et al.* (ref. 26)

Tables 5-11 represented the calculated and experimental solubilities of nitrogen and oxygen in methanol-water, ethanol-water, 1-propanol-water, 2-propanol-water (at 298.15 K) and 1,2-ethanediol-water (at 298.15 K); methane in methanol-water, ethanol-water (at 298.15 K); argon in acetone-water (at 298.15 K) and ethylene in dodecane-hexane (at 293.15 K) solutions. The solubilities are expressed in logarithm of Henry's law constant that were calculated by means of equation (3). It is found that the theory could show qualitative agreement with experimental results. However, there are some discrepancies between calculated and experimental values.

This theory based on Pieritti's approach of scaled particle theory, which is a kind of one parameter first order perturbation theory in which the Percus-Yevick compressibility equation of state for rigid hard sphere mixture is used as a reference and theory assumes pair-wise additively for system energy. This hypothesis is strictly valid for the hard sphere mixtures. However, for real solutions, interactions higher than three-body system must be considered. Therefore, use of hypothesis does not take into account the introduction of gas molecules into the mixed solvent would have some influence on the intermolecular interactions between solvent molecules.

This kind of statistical mechanical theory cannot give the entropy term associated with attractive potential in this case. This can be seen from the fact that the radial distribution functions considered are those rigid hard sphere mixtures. As a result, the contribution from the liquid structure is taking into account only by intermolecular repulsion forces. Although this was found to apply to simple liquids, both alcohol and water are polar associated liquids. Therefore, they may form highly non-ideal solutions, when they are brought together. Moreover, when gases are dissolved in them, the thermodynamic behaviors may become complex. This can be seen from solubility curves. It is natural to consider that the abnormality originates mainly from the hydrogen bonds between like or unlike molecules in the solvent, since in the mixture of alcohol and water, the hydrogen bond probably plays an important role in the thermodynamic behavior³⁵. The entropy associated with hydrogen bonds that are very important in alcohol-water mixtures as well as other attractive forces could not be enumerated at all. Besides neither Pieritti's approach of scaled particle theory nor any other statistical mechanical theory can take into account even the internal energy attributed to hydrogen bond since they have not yet been analytically formulated.

Table 5. Solubilities in terms of logarithm of Henry's law constant ($\ln K_H/\text{atm}$) of nitrogen gas dissolved in methanol (a) + water (b) and ethanol (a) + water (b) at 293.15 K and 1 atmosphere pressure

Methanol mole fraction (x_a)	Expt. $\ln K_H^i$ / atm	Methanol mole fraction (x_a)	Density at 293.15K	Calc. $\ln K_H^i$ / atm	Ethanol mole fraction (x_a)	Expt. $\ln K_H^i$ / atm	Methanol mole fraction (x_a)	Density at 293.15K	Calc. $\ln K_H^i$ / atm
0.0000	11.2185	0.0000	0.9982	11.2882	0.0000	11.2180	0.0000	0.9982	11.2882
0.0274	11.1390	0.0057	0.9965	11.2754	0.0071	11.1280	0.0202	0.9894	11.2689
0.0514	11.0680	0.0287	0.9896	11.2229	0.0199	11.0680	0.0416	0.9819	11.2583
0.0670	11.0460	0.0588	0.9815	11.1587	0.0558	10.9450	0.0890	0.9686	11.2360
0.0967	11.0974	0.0903	0.9740	11.0972	0.0815	10.8930	0.1435	0.9538	1.1487
0.1633	10.9330	0.1232	0.9680	11.0520	0.1015	10.8450	0.2068	0.9352	10.9476
0.2084	10.8530	0.1578	0.9592	10.9596	0.1558	10.6590	0.2811	0.9138	10.6390
0.2931	10.5660	0.1942	0.9515	10.8834	0.2757	10.0690	0.3697	0.8911	10.2389
0.4050	10.2715	0.2716	0.9343	10.6650	0.3206	9.8570	0.4771	0.8677	9.7544
0.5038	9.8521	0.3599	0.9152	10.3844	0.4628	9.2960	0.6100	0.8433	9.1844
0.6088	9.4803	0.4575	0.9846	10.0545	0.5952	8.8430	0.7787	0.8180	8.5168
0.6784	9.2390	0.5675	0.8715	9.6453	0.7130	8.5460	1.0000	0.7893	7.7262
0.7630	8.9450	0.6922	0.8469	9.1780	0.8746	8.1940			
0.8973	8.5903	0.8350	0.8202	8.6468	0.9140	8.1077			
1.0000	8.3670	0.9144	0.8062	8.3615	1.0000	7.9120			
		1.0000	0.7917	8.0634					

[†]Tokunaga (ref. 28)

Table 7. Solubilities in terms of logarithm of Henry's law constant ($\ln K_H/\text{atm}$) of nitrogen and oxygen gases dissolved in 1, 2-ethanediol(a) + water(b) at 298.15 K and 1 atmosphere pressure

1, 2- Ethanediol mole fraction (x_B)	Density at 298.15K ^j	Expt. $\ln K_H/\text{atm}$ (N_2) ⁱ	1, 2- Ethanediol mole fraction (x_B)	Calc. $\ln K_H$ /atm (N_2)	Density at 298.15K ^j	Expt. $\ln K_H/\text{atm}$ (O_2) ⁱ	Calc. $\ln K_H$ /atm (O_2)
0.0000	0.7791	11.3450	0.0000	11.6238	0.9971	10.6652	11.2146
0.0085	1.0009	11.3482	0.0354	11.6230	1.0116	10.6787	11.1864
0.0325	1.0106	11.3644	0.0775	11.6140	1.0260	10.7056	11.1356
0.1146	1.0377	11.3858	0.1185	11.5437	1.0388	10.7126	11.0894
0.1852	1.0540	11.3600	0.1795	11.4260	1.0534	10.6984	10.9826
0.2444	1.0658	11.2946	0.3234	11.3207	1.0770	10.5750	10.6503
0.3130	1.0757	11.2067	.42.42	11.1526	1.0867	10.4246	10.3549
0.4197	1.0864	11.0480	0.5404	10.7377	1.0944	10.2220	9.9933
0.7333	1.1036	10.5668	0.7337	9.8450	1.1037	9.9505	9.4120
1.0000	1.1099	10.2262	1.0000	9.0301	1.1099	9.5793	8.6340

^jYamamoto and Tokunaga (ref. 29)

Table 8. Solubilities in terms of logarithm of Henry's law constant ($\ln K_H/\text{atm}$) of Oxygen gas dissolved in methanol(a) + water(b) and ethanol(a) + water(b) at 293.15 K and 1 atmosphere pressure

Methanol mole fraction (x_a)	Expt. $\ln K_H^i / \text{atm}$	Methanol mole fraction (x_a)	Density at 293.15K	Calc. $\ln K_H / \text{atm}$	Ethanol mole fraction (x_a)	Expt. $\ln K_H^i / \text{atm}$	Methanol mole fraction (x_a)	Density at 293.15K	Calc. $\ln K_H / \text{atm}$
0.0000	10.5580	0.0000	0.9982	10.8193	0.0000	10.5558	0.0000	0.9982	10.8197
0.0188	10.4342	0.0057	0.9965	10.8114	0.0801	10.2183	0.0202	0.9894	10.7996
0.0492	10.2785	0.0287	0.9896	10.7586	0.1058	10.2034	0.0416	0.9819	10.7874
0.0907	10.1542	0.0588	0.9815	10.6986	0.2057	9.9427	0.0890	0.9686	10.7617
0.1103	10.1886	0.0903	0.9740	10.6410	0.3085	9.4254	0.1435	0.9538	10.6772
0.1564	10.2327	0.1232	0.9680	10.5982	0.4052	8.9960	0.2068	0.9352	10.4893
0.2066	10.1696	0.1578	0.9592	10.5128	0.5280	8.5790	0.2811	0.9138	10.2030
0.3064	9.8255	0.1942	0.9515	10.4363	0.5976	8.3570	0.3697	0.8911	9.8323
0.3976	9.5032	0.2716	0.9343	10.2416	0.7171	8.0620	0.4771	0.8677	9.3830
0.4895	9.2090	0.3599	0.9152	9.9851	0.8065	7.8440	0.5398	0.8556	8.8523
0.5927	8.8608	0.4575	9846.0000	9.6781	0.9382	7.5653	0.6100	0.8434	8.5555
0.7046	8.5272	0.5675	0.8715	9.3012	1.0000	7.4030	0.7787	0.8180	8.2328
0.8010	8.2763	0.6922	0.8469	8.8703			1.0000	0.7893	7.4960
0.8923	8.0455	0.8350	0.8202	8.3796					
0.9426	7.9338	0.9144	0.8062	8.1156					
1.0000	7.7832	1.0000	0.7917	7.8395					

Table 10. Solubilities in terms of logarithm of Henry's law constant ($\ln K_{H^i}/\text{atm}$) of methane gas dissolved in methanol(a) + water(b) and ethanol(a) + water(b) at 293.15 K and 1 atmosphere pressure

Methanol mole fraction (x_a)	Expt. $\ln K_{H^i}/\text{atm}$	Methanol mole fraction (x_a)	Density at 293.15K	Calc. $\ln K_{H^i}/\text{atm}$	Ethanol mole fraction (x_a)	Expt. $\ln K_{H^i}/\text{atm}$	Methanol mole fraction (x_a)	Density at 293.15K	Calc. $\ln K_{H^i}/\text{atm}$
0.0000	10.5400	0.0000	0.9982	10.1652	0.0000	10.5400	0.0000	0.9982	10.1652
0.0650	10.2035	0.0287	0.9896	10.0862	0.0260	10.3287	0.0202	0.9894	10.1359
0.1386	10.0257	0.0588	0.9815	9.9904	0.0609	10.1581	0.0416	0.9819	10.1137
0.2016	9.8934	0.0903	0.9740	9.9132	0.1170	9.9650	0.0890	0.9686	10.0664
0.2983	9.5178	0.1232	0.9680	9.8364	0.2432	0.2779	0.1435	0.9538	9.9548
0.4871	8.7933	0.1942	0.9515	9.6168	0.3112	8.9464	0.2068	0.9352	9.7292
0.6011	8.3428	0.2716	0.9343	9.3621	0.5285	7.9444	0.2811	0.9138	9.3970
0.6762	8.0520	0.3599	0.9152	9.0419	0.7601	7.2225	0.3697	0.8911	8.9728
1.0000	7.0290	0.4575	0.9846	8.6686	1.0000	6.6372	0.4771	0.8677	8.4630
		0.5675	0.8715	8.2228			0.5398	0.8556	8.1784
		0.6922	0.8469	7.7218			61001.0000	0.8434	7.8662
		0.8350	0.8202	7.1609			0.6891	0.8310	7.7353
		0.9144	0.8062	6.8590			0.7787	0.8180	7.1733
		1.0000	0.7917	6.5526			1.0000	0.7893	6.3590

^kTokunaga and Kawai (ref. 30)

Table 11. Solubilities in terms of logarithm Henry's law constant ($\ln K_H/\text{atm}$) of argon gas dissolved in acetone(a) + water(b) at 298.15 K and ethylene in dodecane(a) + hexane(b) at 293.15 K and 1 atmosphere pressure.

Acetone mole fraction (x_a)	Density at 298.15K ^l	Expt. $\ln K_H^i / \text{atm}$	Calc. $\ln K_H / \text{atm}$	Dodecane. Mole fraction (x_n)	Expt. $\ln K_H^m / \text{atm}$	Dodecane mole fraction (x_n)	Density at 298.15K ^m	Calc. $\ln K_H / \text{atm}$
0.0000	0.9976	10.6534	10.5509	0.0000	3.8776	0.0000	0.6552	3.7220
0.0045	0.9951	10.6133	10.5436	0.1550	3.8776	0.0600	0.6650	3.7587
0.0253	0.9865	10.4838	10.5326	0.2610	3.8825	0.1267	0.6748	3.7933
0.0367	0.9821	10.4726	10.5208	0.2960	3.8873	0.1978	0.6834	3.8092
0.0601	0.9735	10.3747	10.4850	0.3670	3.8825	0.2772	0.6812	3.8078
0.0882	0.9640	10.2682	10.4252	0.4420	3.8873	0.3652	0.7013	3.8365
0.1448	0.9456	9.9888	10.2398	0.7220	3.8776	0.4632	0.7089	3.8184
0.1908	0.9307	9.7090	10.0303	0.8170	3.8444	0.5731	0.7181	3.8189
0.2643	0.9092	9.3230	9.7152	1.0000	3.8351	0.8381	0.7367	3.7855
0.3982	0.8959	8.7035	9.0332			1.0000	0.7450	3.7493
0.5157	0.8518	8.4053	8.4667					
0.6266	0.8336	7.9065	7.9958					
0.7037	0.8229	7.6998	7.6998					
0.8497	0.8047	7.3686	7.1894					
1.0000	0.7854	7.0352	6.6922					

^lYamamoto and Tokunaga (ref. 31); ^mSahgal and Hayduk (ref. 32)

In addition, for carrying out the computations, various kinds of other physical parameters are needed. Among these, the rigid hard sphere diameter of the water and alcohols are most important. However, the value of hard sphere diameter of solvent and solute available in the literature may be calculated from the surface tension, viscosity, second virial coefficient, enthalpy of vaporization, molecular dynamic simulation and gas solubility etc. The results obtained from different sources are not unique, e.g., σ_{methanol} 3.835 (ref. 21), 3.71 & 3.67 (ref.17), 4.082 (ref. 35) 3.69 (ref. 22) for σ_{ethanol} 4.435 (ref. 21) 4.36 & 4.31(ref. 17), 4.686 (ref. 35), 4.34 (ref. 22) and for water 2.77 (ref. 17) 2.76, 2.75 (ref.16), 2.86 (ref. 25) 2.89 (ref. 34) 2.56 & 2.922 (ref. 36), all values are in Angstroms unit. So, exact choice of this parameter is too much difficult. The quantitative disagreement between experimental and theoretical solubilities may be considered to be partly due to this problem.

However, the present statistical mechanical theory is able to explain qualitatively the experimental solubilities of single non-polar gas in mixed solvents. From the above discussion, it is interesting to conclude the general behavior of gas solubility.

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