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Solubilities of Ethylene, Ethane, and Carbon Dioxide in Mixed Solvents Consisting of Methanol, Acetone, and Water[1]

S. Zeck[2] and H. Knapp[2]

The amount of gas absorbed in a liquid solvent or solvent mixture is measured with a high-precision gas burette. Solubility coefficients (Henry and Ostwald coefficients) of C_2H_4 and C_2H_6 are determined at ambient temperature and atmospheric pressure (1) in the pure solvents C_3H_6O, CH_3OH, and H_2O; (2) in the three binary mixtures of the solvents as a function of the composition of the solvent mixture; and (3) in several ternary mixtures of arbitrary composition. The experimental data are presented in diagrams and tables.

KEY WORDS: absorption; gas solubility; Henry coefficients; liquid solvents and solvent mixtures; Ostwald coefficients.

1. INTRODUCTION

The knowledge of the solubility of gases in liquid solvents is important as a basis for the design of separation processes as well as for the development of molecular models of dilute solutions. There are three aspects which are of interest.

(i) How much gas is dissolved in a liquid at a relatively low pressure? Henry coefficients must be determined approaching the state of infinite dilution in the liquid. If the temperature dependence of the Henry coefficients is known, the heat of the solution can be calculated.

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[2] Institute of Thermodynamics and Plant Design, Technical University of Berlin, 1000 Berlin 12, Federal Republic of Germany.

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(ii) What are the conditions in high-pressure systems (10–100 bar) where components of a gas mixture are selectively absorbed in a solvent or solvent mixture? Multicomponent vapor–liquid equilibria must be investigated over a wide range of temperatures and pressures.

(iii) What is the concentration of the low volatile solvent in a high-pressure gas phase? Special experimental techniques must be applied to detect and to determine trace quantities.

All three aspects can be studied in special experimental equipment in our laboratory.

The solubility of various gases in various liquid solvents has been studied for more than a hundred years. Experimental data have been collected and are presented in several reference books.

Most of the measurements have been made with pure solvents. Only very few publications report on the solubilities of gases in solvent mixtures. It would be very helpful to have available more experimental information on the effect of the composition in mixed solvents as, on the one hand, many technical gaseous systems are operated with mixed solvents and, on the other hand, our theoretical understanding of the conditions in liquid solutions needs improvement. It would also be important to investigate the effect of water in mixed solvents as, on the one hand, water often is present in volvent mixtures and, on the other hand, the special molecular structure of water calls for special theoretical attention.

For these reasons we have decided to measure the solubility of several gases is solvent mixtures containing methanol, acetone, and water (see Table I).

Table I. Summary of the Experimental Program for Gas Solubilities

Components			
Solvent	Solute	T (K)	Number of points
$C_3H_6O-CH_3OH$	C_2H_4	298.15	11
$C_3H_6O–CH_3OH$	C_2H_6	298.15	10
$C_3H_6O–H_2O$	C_2H_4	298.15	14
$C_3H_6O–H_2O$	C_2H_6	298.15	14
$CH_3OH–H_2O$	C_2H_4	298.15	13
$CH_3OH–H_2O$	C_2H_6	298.15	14
$CH_3OH–H_2O$	CO_2	293.15	4
$C_3H_6O–CH_3OH–H_2O$	C_2H_4	298.15	7
$C_3H_6O–CH_3OH–H_2O$	C_2H_6	298.15	7

2. APPARATUS

A schematic flow diagram of the equipment is shown in Fig. 1. A detailed description of the apparatus, of the experimental procedure, and of the data reduction is presented elsewhere [1]. It should be pointed out here, perhaps, that the investigation of solvent mixtures requires additional procedures. The amount of solvent in the equilibrium cell can be determined originally by weighing. The original composition of the liquid mixture, however, changes during the degassing of the solvent due to the different volatilities of the components in the solvent mixture. Samples must therefore be taken and analyzed in the gas chromatograph (GC) or in the densimeter. The vapor pressure of the solvent mixture is very low; however, it must be considered for an accurate data reduction. The Wilson equation was used to calculate the activity coefficients.

Considering all errors in the measurement of temperature, pressure, density, volume, and concentration, we believe that the total inaccuracy is smaller than ±0.5%. The reproducibility obtained in repeated measurements was within ±0.3%.

3. PROPERTIES OF SUBSTANCES

For proper data reduction, information is required about the thermophysical properties of the pure substances and of the solvent mixtures. Some of the values were taken from the literature, some measured in our

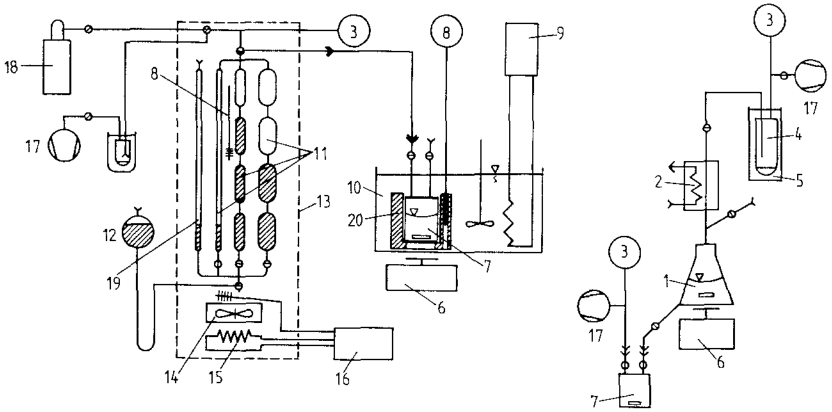

Fig. 1. Schematic flow diagram of solubility apparatus with degassing section. 1, Flask for degassing; 2, water cooler; 3, vacuum gauge; 4, cold trap; 5, Dewar with liquid nitrogen; 6, magnetic stirrer; 7, equilibrium cell; 8, thermometer; 9, thermostat; 10, liquid bath; 11, precision burette; 12, mercury container; 13, air bath; 14, fan; 15, heater; 16, temperature controller; 17, vacuum pump; 18, solute gas supply; 19, mercury manometer; 20, copper shell.

own lab, and some calculated with available correlations. All the data that are needed are listed in Ref. 1.

The densities of the three binary solvent mixtures were determined in the Anton Paar densimeter DMA 602 (Graz, Austria). From the densities the excess volumes v^E were calculated as $cm^3 \cdot mol^{-1}$ and correlated by a Redlich–Kister polynomial.

$$v^E = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{(i-1)} \tag{1}$$

The coefficients of the Redlich–Kister polynomial are given in Table II. The measurements could be compared with published data for all three mixtures; the agreement is very good.

Activity coefficients for the binary and ternary solvent mixtures were calculated with the g^E model proposed by Wilson [2] with binary interaction parameters taken from the Dechema Data Series [3].

4. DATA REDUCTION

As various disciplines of science are interested in the solubility of gases in liquid solvents, various notions have been suggested for the definition of solubility: Ostwald, Bunsen, Kuenen, and Henry coefficients, *K*- value, etc. The results of our measurements are reduced to values of the Ostwald and Henry coefficients. The Ostwald coefficient is defined as [5]:

$$L_0 = V_i^G / V_{0j}^L$$

V_i^G is the volume of gas i dissolved in the volume V_{0j}^L of pure liquid solvent or solvent mixture j at temperature T and pressure p of the system.

The Henry coefficient is defined as

$$H_{ij}(T, p_{0j}^{LV}) = f_i / x_i \qquad \text{for} \quad x_i \to 0$$

Table II. Coefficients of the Redlich–Kister Polynomial Calculated with Eq. (1)

System	A_1	A_2	A_3	A_4	RMS[a] ($cm^3 \cdot mol^{-1}$)
C_3H_6O–CH_3OH	−1.40856	0.28903	−0.15715	—	0.0041
C_3H_6O–H_2O	−5.78844	2.18152	−0.76631	—	0.0170
CH_3OH–H_2O	−4.04742	0.32763	0.63860	−0.80802	0.0093

[a] Root mean square.

x_i is the concentration of solute i in mole fraction in the liquid solution consisting of solute i and solvent j, and f_i is the fugacity of solute i in the gaseous phase-extrapolated for the state of infinite dilution of solute i in the liquid phase.

Since solubility coefficients cannot be measured directly in the equilibrium apparatus, the directly observed or primary variables must be reduced based on the knowledge of more thermophysical properties. Details of the procedure are given in Ref. 1. In Table III the primary

Table III. List of Primary and Secondary Variables and Thermodynamic Properties Needed for Data Reduction

	Primary variables
T^{B}	Temperature of gas burette, by high-precision mercury (Hg) thermometer
T^{C}	Temperature of equilibrium cell, by platinum-resistance thermometer (PT-100)
p	System pressure, by Hg manometer
m_j	Mass of solvent or solvent mixture by scale
x_j	Concentration of solvent $j = 1$ and 2 in solute-free solvent mixture $x_j = n_j/\sum n_j$, by gas chromatography (GC) or densimeter
V_i^{B}	Volume of solute i displaced from gas burette (11), voluminetrically at T^{B} and p
	Thermophysical properties
M	Molar mass of solute i and solvents j
v_{0j}^{L}	Molar volume of solvents
v_{0i}^{G}	Molar volume of solute i, $v_{0i}^{\mathrm{G}} = (RT/p) + B_{ii}$
φ_i	Fugacity coefficient of solute i in gaseous mixture in equilibrium cell, $\ln \varphi_i = (p/RT)(2 \sum_k y_k B_{ik} - B_{\mathrm{M}})$
p_{0j}^{LV}	Vapor pressure of solvent or solvent mixture j
$v_{\infty i}^{\mathrm{L}}$	Partial molar volume of gas i at infinite dilution
	Secondary variables
y_i	Concentration in mole fraction of i in gaseous mixture in V^{CG}, $(1 - y_j)$
V^{CG}	Residual gas volume in cell (7), $(V^{\mathrm{C}} - V^{\mathrm{CL}})$
V^{CL}	Volume of liquid solution in cell $V^{\mathrm{CL}} = n_j v_j^{\mathrm{L}} + n_i v_i^{\mathrm{L}}$, where $v_j^{\mathrm{L}} \approx \sum_j x_j v_{0j}$ and $v_i^{\mathrm{L}} \approx v_{\infty i}^{\mathrm{L}}$
V^{C}	Total volume of cell
x_i	Concentration in mole fraction of solute i in solution $n_i/(n_i + \sum_j n_j)$
γ_i^*	Unsymmetrical activity coefficient $\ln \gamma_i^* = (A/RT)[(1 - x_i)^2 - 1]$
V_i^{G}	Volume of solute i absorbed, $(V_i^{\mathrm{B}} - y_i V^{\mathrm{CG}})$
V_{0j}^{L}	Volume of pure solvent or solvent mixture, $n_j v_{0j}^{\mathrm{L}}$
n_i	Quantity of solute absorbed in solution $V_i^{\mathrm{G}}/v_{0i}^{\mathrm{G}}$
n_j	Quantity of solvent or solvent mixture $m_j/\sum_j x_j M_j$

variables, the methods of measurements, the required thermophysical properties, and the secondary variables are presented. Finally, with these variables the suggested values of the Ostwald and Henry coefficients can be calculated.

$$H_{ij}(T, p_{0j}^{\mathrm{LV}}) = \varphi_i y_i p/(x_i \gamma_i^* \pi_i^*) \qquad \text{where} \quad \ln \pi_i^* = v_{\infty i}^{\mathrm{L}}/(RT)(p - p_{0j}^{\mathrm{LV}}) \tag{2}$$

5. RESULTS

5.1. Solubilities in Binary Solvent Mixtures

Henry and Ostwald coefficients for one solute gas in a binary solvent mixture are presented in Table IV and Figs. 2 and 3 as a function of the composition of the solvent mixture. The presentations include the solubilities in each of the pure solvents. The figures also show the deviation of the Henry coefficient on a logarithmic scale (sometimes called the "excess Henry coefficient").

$$\ln H_{i,\mathrm{MIX}}^{\mathrm{E}} = \ln H_{i,\mathrm{MIX}} - \sum_{j=1}^{2} x_j \ln H_{ij} \tag{3}$$

with solvent j ($j = 1, 2$) or solvent mixture MIX and solute i ($i = 3$). For one selected example the Ostwald coefficient and the excess Ostwald coefficient

$$\ln L_{i,\mathrm{MIX}}^{\mathrm{E}} = \ln L_{i,\mathrm{MIX}} - \sum_{j=1}^{2} \phi_j \ln L_{ij} \tag{4}$$

are plotted in Fig. 4 as a function of the volumetric composition, where the volume fraction is

$$\phi_j = (x_j v_{0j}) \bigg/ \left(\sum_{j=1}^{2} x_j v_{0j} \right) \tag{5}$$

The extraordinary behavior of the water-rich side in the solution noticeable in the plots of the Henry coefficient disappears in this presentation. This observation seems to indicate that the molar volumes of the two solvents should be considered in correlations for the solubility in solvent mixtures [6, 7].

5.2. Solubilities in Ternary Solvent Mixtures

The results for the ternary solvent mixtures are presented in Table V. In addition, calculated vapor pressures [3] and measured densities for the ternary solvent mixtures are given.

Table IV. Experimental Points for Gas Solubilities of C_2H_4 and C_2H_6 in Binary Solvent Mixtures at $T = 298.15$ K

Acetone (1)–methanol (2)–C_2H_4			Acetone (1)–methanol (2)–C_2H_6		
x_1 (mol · mol^{-1})	$H_{i,\mathrm{MIX}}$ (bar)	$L_{i,\mathrm{MIX}}$ (—)	x_1 (mol · mol^{-1})	$H_{i,\mathrm{MIX}}$ (bar)	$L_{i,\mathrm{MIX}}$ (—)
1.0000	91.86	3.707	1.0000	102.76	3.294
0.9322	97.80	3.594	0.9322	109.24	3.188
0.7764	110.88	3.421	0.7764	125.04	3.023
0.7477	113.47	3.392	0.6144	143.17	2.877
0.6144	127.94	3.227	0.4954	159.05	2.770
0.4962	142.20	3.101	0.3886	174.19	2.696
0.3886	156.90	2.996	0.2526	198.97	2.572
0.2497	180.71	2.840	0.1665	215.93	2.512
0.1665	196.72	2.758	0.1085	228.87	2.467
0.1085	212.03	2.663	0.0000	253.64	2.411
0.000	239.27	2.555			

Acetone (1)–water (2)–C_2H_4			Acetone (1)–water (2)–C_2H_6		
x_1 (mol · mol^{-1})	$H_{i,\mathrm{MIX}}$ (bar)	$L_{i,\mathrm{MIX}}$ (—)	x_1 (mol · mol^{-1})	$H_{i,\mathrm{MIX}}$ (bar)	$L_{i,\mathrm{MIX}}$ (—)
1.0000	91.86	3.707	1.0000	102.76	3.294
0.8995	114.07	3.227	0.8995	131.44	2.786
0.8010	143.14	2.802	0.8010	168.80	2.364
0.6528	209.03	2.221	0.6545	258.31	1.786
0.5841	266.73	1.877	0.5841	338.25	1.474
0.4858	381.40	1.478	0.5771	347.57	1.446
0.3919	617.69	1.036	0.4943	491.52	1.130
0.2805	1217.40	0.6245	0.3815	890.06	0.7277
0.1960	2304.10	0.3828	0.2891	1801.60	0.4146
0.0989	5558.10	0.1928	0.1973	3783.20	0.2318
0.0949	5651.90	0.1912	0.0915	12300.00	0.0882
0.0445	8613.30	0.1410	0.0431	20255.00	0.0598
0.0238	9645.80	0.1322	0.0221	24498.00	0.0518
0.0000	11490.00	0.1178	0.0000	29600.00	0.0456

Methanol (1)–water (2)–C_2H_4			Methanol (1)–water (2)–C_2H_6		
x_1 (mol · mol^{-1})	$H_{i,\mathrm{MIX}}$ (bar)	$L_{i,\mathrm{MIX}}$ (—)	x_1 (mol · mol^{-1})	$H_{i,\mathrm{MIX}}$ (bar)	$L_{i,\mathrm{MIX}}$ (—)
1.0000	239.27	2.555	1.0000	253.64	2.411
0.9034	315.06	2.058	0.9034	343.03	1.888
0.7983	432.69	1.604	0.7983	498.70	1.388
0.6999	623.58	1.191	0.6999	737.28	1.005
0.6051	877.82	0.9078	0.6059	1124.00	0.7061
0.5025	1346.70	0.6401	0.5038	1865.50	0.4602
0.4114	2101.50	0.4420	0.4112	3206.90	0.2884
0,3103	3465.30	0.2917	0.3084	6025.10	0.1674
0.2088	5625.30	0.1965	0.2095	10964.40	0.1003
0.1070	8058.70	0.1509	0.1508	14862.00	0.0782
0.0541	9420.80	0.1358	0.1061	18040.20	0.0671
0.0254	10232.40	0.1288	0.0528	23000.00	0.0555
0.0000	11490.00	0.1178	0.0241	25578.10	0.0514
			0.0000	29600.00	0.0456

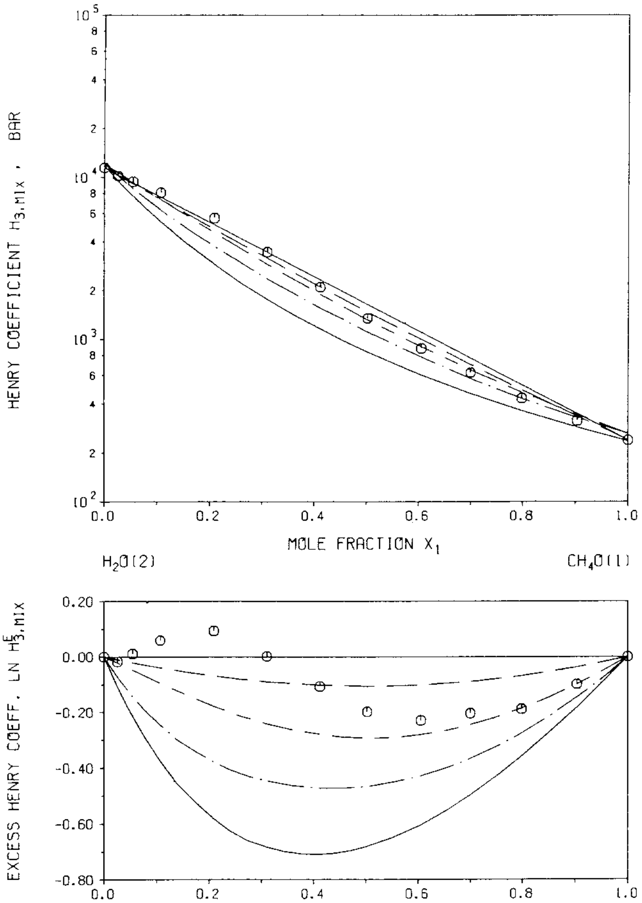

Fig. 2. Henry coefficient and excess Henry coefficient for ethylene in a mixture of methanol and water. Solvent: (1) methanol, CH_4O; (2) water, H_2O. Solute: (3) ethylene, C_2H_4. Temperature, 298.15 K. Experimental points (○), Th. TU Berlin. Calculated (——) by UNIFAC; (–·–·–) by GCEOS; (– – –) by GCEOS (v^E); (— — —) by two-syffix Margules.

6. COMPARISON WITH OTHER PUBLISHED DATA

Often it is not possible to make a comparison with published data, as information is missing on the exact conditions under which original measurements were taken. There are solubility data for gases in the pure solvents. The results are listed in Table VI and can be compared with our

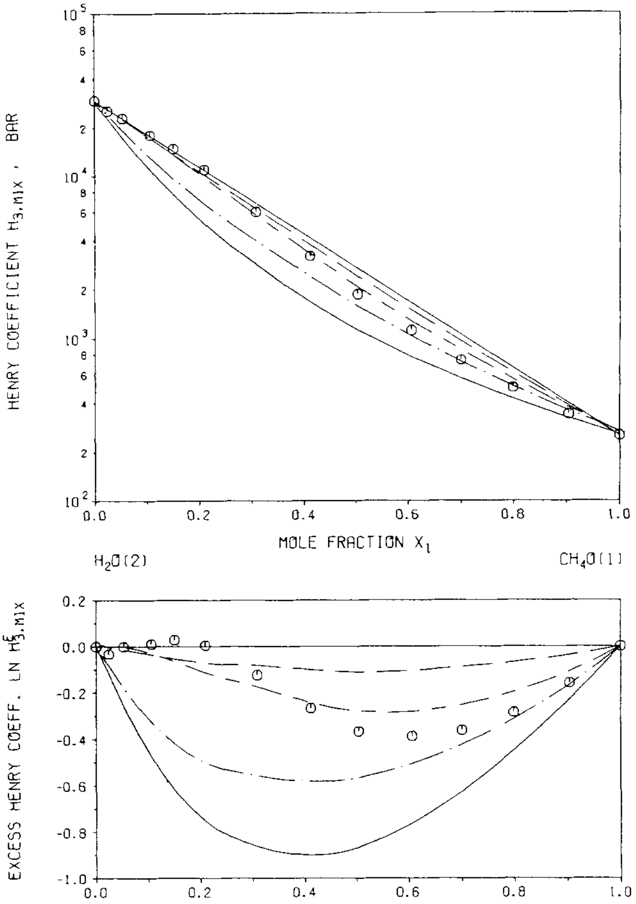

Fig. 3. Henry coefficient and excess Henry coefficient for ethane in a mixture of methanol and water. Solvent: (1) methanol, CH_4O; (2) water, H_2O. Solute: (3) ethane, C_2H_6. Temperature, 298.15 K. Experimental points (○), That. TU Berlin. Calculated (——) by UNIFAC; (–·–·–) by GCEOS; (-----) by GCEOS (v^E); (– – – –) by two-suffix Margules.

data. Only a few results are published on solubilities in solvent mixtures. Comparisons are presented in Fig. 5.

7. CORRELATIONS

At present it is not possible to predict accurately solubilities in organic solvents or water from molecular theory alone. The group contribution methods permit some predictability for organic solvents that can be assem-

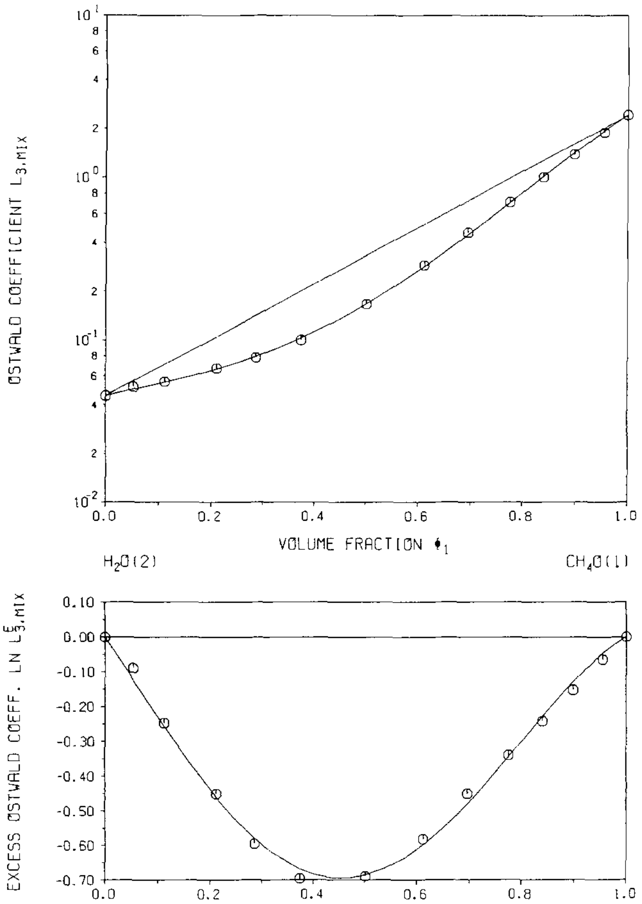

Fig. 4. Ostwald coefficient and excess Ostwald coefficient for ethane in a mixture of methanol and water. Solvent: (1) methanol, CH_4O; (2) water, H_2O. (3) ethane, C_2H_6. Temperature, 298.15 K. Experimental points (○), That. TU Berlin. Calculated (——), fit. eq.

bled of molecular subgroups [14–17]. Otherwise correlations must contain adjustable parameters that are fitted to experimental data.

Empirical and semiempirical correlations—if applicable at all to gas solubilities—should present the solubility in a pure solvent accurately. The crucial test is the representation of the solubility in a solvent mixture as a function of the composition.

Three "popular" correlations were selected for comparison of experimental and calculated data in solvent mixtures:

Table V. Experimental Points for Gas Solubilities of C_2H_4 and C_2H_6 in Ternary Solvent Mixtures at $T = 298.15$ K, p^{LV} and v of solvant mixture without solute

Solvent: (1) Acetone, C_3H_6O
(2) Methanol, CH_4O
(3) Water, H_2O
Solute: (4) Ethylene, C_2H_4

x_1 (mol · mol^{-1})	x_2 (mol · mol^{-1})	$H_{i,\text{MIX}}$ (bar)	$L_{i,\text{MIX}}$ (—)	pLV^a (mbar)	v^b (cm^3 · mol^{-1})
0.3318	0.3367	348.49	1.651	240.85	42.974
0.1006	0.8022	270.16	2.220	201.49	41.379
0.1981	0.6005	309.11	1.911	221.27	41.867
0.7983	0.1028	124.72	3.110	292.63	64.557
0.6129	0.1928	177.65	2.514	275.77	55.736
0.2019	0.2009	1058.3	0.7153	209.49	32.497
0.0995	0.1043	3587.2	0.2734	162.64	25.015

Solvent: (1) Acetone, C_3H_6O
(2) Methanol, CH_4O
(3) Water, H_2O
Solute: (4) Ethane, C_2H_6

x_1 (mol · mol^{-1})	x_2 (mol · mol^{-1})	$H_{i,\text{MIX}}$ (bar)	$L_{i,\text{MIX}}$ (—)	pLV^a (mbar)	v^b (cm^3 · mol^{-1})
0.3318	0.3367	440.24	1.302	240.85	42.974
0.1006	0.8022	301.44	1.987	201.49	41.379
0.1982	0.6005	363.10	1.625	221.27	41.867
0.7983	0.1028	144.06	2.680	292.63	64.557
0.6129	0.1928	209.54	2.123	275.77	55.736
0.2019	0.2009	1520.8	0.4958	209.49	32.497
0.0995	0.1043	6549.3	0.1492	162.64	25.015

[a] Calculated with the Wilson equation [2].
[b] Measured with a U-tube densimeter.

Table VI. Comparison of Our Own Gas Solubility Data in Pure Solvents with Literature Values at $T = 298.15$ K

System	L_0 (this work)	L_0 (lit. values)	Ref. No.
C_2H_4–C_3H_6O	3.631_a	3.640	4
C_2H_6–C_3H_6O	3.227^a	3.225	4
C_2H_6–CH_3OH	2.381^a	2.379	8
		2.34 ± 0.09	9
C_2H_4–H_2O	0.1175^a	0.1174	10
C_2H_6–H_2O	0.0456	0.0453	11

[a] Reduced by assuming ideal behavior of gas and liquid phase.

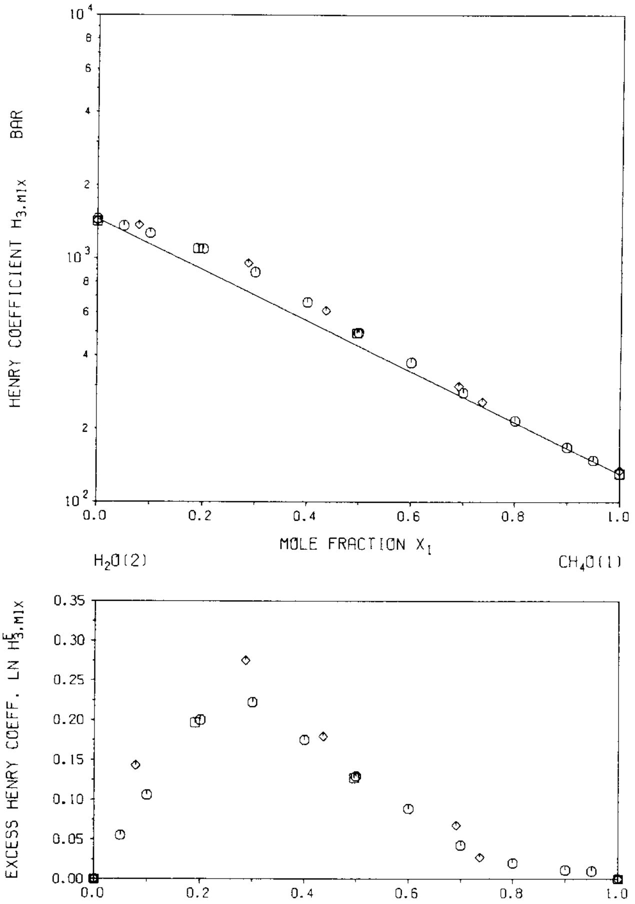

Fig. 5. Comparison of experimental data from this work with literature data. Solvent: (1) methanol, CH_4O; (2) water, H_2O. Solute: (3) carbon dioxide, CO_2. Temperature, 293.15 K. (□) This work; (○) Ref. 12; (◇) Ref. 13.

(i) the two-suffix Margules model [18],

$$\ln H^{E}_{i,\mathrm{MIX}} = \ln H_{i,\mathrm{MIX}} - \sum_{j} x_j \ln H_{ij} = -A_{12} x_1 x_2 \tag{6}$$

for which the binary parameter A_{12} for the solute-free solvent mixture was fitted to experimental VLE data;

(ii) the modified UNIFAC group contribution g^E model [17], for which the pure-component and binary parameters were taken from Ref. 17; and

(iii) the GCEOS (group contribution equation of state) model [19], with binary parameters for the solute-free solvent mixture fitted to VLE *or* v^E data.

The results of the comparison are illustrated in the deviation plots in Figs. 2 and 3.

The calculation of the solubility in the ternary solvent mixture was not satisfactory with any of the three correlations.

8. CONCLUSION

The deviation of Henry and Ostwald coefficients from a straight-line interpolation on a logarithmic scale [defined in Eqs. (3) and (4)] can be plotted as a function of the mole fraction or of the volume fraction. In a binary solvent mixture in systems containing water, the dependence on the volume fraction seems to be more adequate [6, 7, 20] (compare Figs. 2 and 3 with Fig. 4). This observation is supported by the fact that the GCEOS model gives a better prediction of the solubility in systems containing water when volumetric (v^E) data on the solvent mixture instead of VLE data are taken into consideration (see Figs. 2 and 3).

The models which usually represent the excess functions in binary or ternary mixtures with a good accuracy seem to fail in systems consisting of one low-boiling solute and two organic solvents, espcially if one of the components is water. Obviously the models have to be improved for the description of such conditions. Also obviously more experimental data in binary and ternary solvent mixtures are needed to develop better correlations.

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