tional group, the presence of the $CH_3$ and COOC groups, and the interaction parameters given in ref *18*, a mean estimation of the vapor concentrations is obtained of 0.019 (mean error of 5.1%) for methyl propanoate–ethanol and of 0.009 (mean error of 1.4%) for methyl propanoate–propan-1-ol.

In the aggregate, the prediction of the equilibrium data of these methyl propanoate–alkanol systems, both with the ASOG method and with the three cases chosen from the UNIFAC model, is good, with an overall mean error of less than 4% in every case. Neither method can therefore be viewed with more favor than the other, nor can any one case of the three presented by singled out in the case of the UNIFAC model since, with all certainty, the results of the predictions may differ greatly according to the family studied.

The azeotrope found for the system $x\mathrm{H_5C_2COOCH_3} + (1 - x)\mathrm{C_2H_5(OH)}$ corresponds to a value of $x = y = 0.483$ and $T = 345.58$ K, a concentration that differs by, approximately, 7% from that presented by Horsley (*5*). The ASOG group contribution model predicts the azeotrope of the above-mentioned system under conditions of $T = 345.70$ K and $x = y = 0.422$, with an error of 12.6%, while, in the three UNIFAC model cases studied, the azeotrope value closest to the experimental one is achieved, under conditions of $T = 345.55$ K and $x = y = 0.505$, with an error of 4.6% in the estimation of the said singular point.

**Registry No.** EtOH, 64-17-5; PrOH, 71-23-8; methyl propanoate, 554-12-1.

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# Gas Solubilities ($H_2$, He, $N_2$, CO, $O_2$, Ar, $CO_2$) in Organic Liquids at 293.2 K

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**Solubilities of hydrogen, helium, nitrogen, carbon monoxide, oxygen, and carbon dioxide in 25 pure organic liquids and in 2 binary mixtures have been determined at the temperature of 293.2 K. The results are compared to the available literature data, to the regular-solution theory, and to the scaled-particle theory.**

Experimental gas solubilities in organic liquids are tabulated for many gas/liquid systems (*1*). However, in a recent study (*2*) on oxygen diffusivities in organic liquids, some of the data needed to evaluate the diffusivities from the measured transmissibilities were not available. The regular-solution theory and the scaled-particle theory were not always applicable, and in other cases their predictions differed considerably. Therefore, gas solubilities in organic liquids were studied experimentally in 89 different gas/liquid systems and compared to the two models.

## Experimental Section

The gas solubilities were determined by a barometric method used already in a previous study (*3*). The measuring chamber was a glass vessel divided into chambers for the liquid ($V_L$ = 349.6 cm$^3$) and the gas ($V_G$ = 598.9 cm$^3$) by a horizontal glass plate with openings at the center and near the wall. The plate enabled the exact adjustment of the liquid level and inhibited premature gas absorption. The vessel was kept at a temperature of 293.2 ± 0.1 K by means of a jacket connected to a thermostat; furthermore, the apparatus was placed in a box with an internal air temperature of 293.2 ± 0.2 K. The substances were obtained from Merck at the highest available purity except for ligroin (alkanes with a bp range of 373–413 K).

A surplus volume of liquid was degassed by evacuation. The process was terminated once the correct liquid level was reached by evaporation of the liquid at its vapor pressure $P_L$. Dry gas of atmospheric pressure $P_0$ was slowly introduced into the head space. After pressure and temperature equilibration, the gas line was disconnected and a magnetic stirrer in the liquid was started. The liquid overflowed the plate and got

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**Table I. Henry's Constants for $H_2$, $O_2$, and $CO_2$ at 293.2 K**

| liquid | $H$, Pa m$^3$ mol$^{-1}$ $H_2$ | $O_2$ | $CO_2$ |
|---|---|---|---|
| acetone | 27 080 | 9 400 | 347 |
| aniline | 93 870 | 38 480 | 1702 |
| benzene | 33 900 | 11 080 | 946 |
| 1-butanol | 34 870 | 11 390 | 1179 |
| *n*-butyl acetate | 28 430 | 9 360 | 499 |
| carbon tetrachloride | 32 130 | 8 020 | 909 |
| cyclohexane | 29 690 | 8 620 | 1414 |
| decalin | 42 343 | 12 700 | 2001 |
| 1,2-dichloroethane | 44 900 | 15 340 | 650 |
| 1,4-dioxane | 49 110 | 16 320 | 357 |
| ethanol | 29 380 | 10 360 | 802 |
| ethyl acetate | 29 290 | 8 600 | 399 |
| ethylbenzene | 37 480 | 11 160 | 1124 |
| ligroin |  | 7 558 |  |
| methanol | 29 740 | 10 490 | 601 |
| nitrobenzene | 72 370 | 21 970 | 905 |
| 2-propanol | 30 910 | 9 780 | 1070 |
| 1-tetradecene | 35 960 | 10 720 | 1551 |
| tetralin | 51 480 | 16 850 | 1610 |
| 1,2,4-trimethylbenzene | 39 020 | 12 140 | 1251 |
| toluene | 35 960 | 10 670 | 965 |
| *m*-xylene | 34 700 | 10 890 | 1067 |

**Table II. Henry's Constants for He, Ar, $N_2$, and CO at 293.2 K**

| liquid | $H$, Pa m$^3$ mol$^{-1}$ He | Ar | $N_2$ | CO |
|---|---|---|---|---|
| methanol | 85 500 | 10 330 | 17 310 | 12 100 |
| 1,2-dichloroethane | 156 300 | 13 940 | 27 640 | 16 930 |
| toluene | 118 000 | 10 190 | 19 060 | 22 440 |

saturated with the gas within 3–6 min. The decrease of the gas pressure at isochoric and isothermal conditions was measured with a micromanometer (MDC-FC-001, Furness Controls Ltd.) and recorded. A mercury manometer was used in case of very high gas solubility ($CO_2$). The changes in the composition of the liquid mixtures during evacuation were detected by refractometry. When the oxygen solubilities in aniline and tetralin were studied, a slow pressure decrease due to autoxidation occurred, but it was negligible during the short measuring time. More experimental details are reported elsewhere (*4*).

From the total pressure decrease $\Delta P$, Henry's constant $H$ was evaluated according to the relation

$$H = \frac{P_0 - \Delta P - P_L}{\Delta P} RT \frac{V_L}{V_G} \tag{1}$$

The mean values of the oxygen and carbon dioxide solubilities in water compiled in ref *1* were reproduced with ±1% accuracy. The reproducibility in the case of organic liquids was usually also ±1%; at high vapor pressure of the liquid, deviations up to ±2% were encountered in few cases. Each reported value is the mean of three determinations.

## Results and Discussion

The determined Henry's constants are listed in Tables I–III. The results on the oxygen solubility in the liquid mixtures (Table III) are illustrated in Figure 1. Henry's constant runs through a minimum in the cyclohexane/benzene system whereas in the ethanol/toluene system a maximum is encountered. The results could be described in the form (*6*)

$$\ln H = x_1 \ln H_1 + x_2 \ln H_2 - \alpha_{1,2} x_1 x_2 \tag{2}$$

$H_1$ and $H_2$ are Henry's constants in the pure liquids 1 and 2, respectively, and $x_1$ and $x_2$ are the mole fractions of the liquids in the mixture. The expansion factor $\alpha_{1,2}$ was fitted to the experimental data by nonlinear regression analysis. The optimum values of +0.41 for cyclohexane/benzene and −0.14 for ethanol/toluene describe the measured oxygen solubilities rather well except for low ethanol mole fractions (Figure 1).

**Table III. Henry's Constants for Oxygen in Mixtures of Organic Liquids at 293.2 K**

| cyclohexane/benzene mixtures: mole fracn cyclohexane | $H$, Pa m$^3$ mol$^{-1}$ | ethanol/toluene mixtures: mole fracn ethanol | $H$, Pa m$^3$ mol$^{-1}$ |
|---|---|---|---|
| 0 | 11 080 | 0 | 10 670 |
| 0.067 | 10 550 | 0.050 | 10 920 |
| 0.134 | 9 990 | 0.136 | 10 950 |
| 0.315 | 9 410 | 0.280 | 10 880 |
| 0.540 | 8 850 | 0.550 | 10 770 |
| 0.785 | 8 430 | 0.735 | 10 720 |
| 0.900 | 8 540 | 0.885 | 10 540 |
| 1 | 8 620 | 0.943 | 10 380 |
|  |  | 1 | 10 360 |

**Table IV. Mean Relative Deviations of Literature Data and Model Predictions from Experimental Results in Tables I and II**

| gas | mean relative deviation,[a] % lit data (*1*) | regular-solution theory (*6*) | scaled-particle theory (*7*) |
|---|---|---|---|
| $H_2$ | 7.4 (16) | 16.7 (10) | 7.2 (9) |
| He | 9.5 (2) |  | 63.8 (2) |
| $N_2$ | 4.9 (2) | 10.6 (1) | 27.9 (2) |
| CO | 5.7 (2)[b] | 16.4 (1) |  |
| $O_2$ | 6.3 (12) | 12.0 (10) | 52.7 (9) |
| Ar | 8.4 (2) | 2.7 (1) | 67.8 (2) |
| $CO_2$ |  | 32.1 (10) | 52.2 (9) |
| mean | 7.0 (36) | 19.2 (33) | 40.2 (33) |

[a] Number of G/L systems in parentheses. [b] Reported by Wilhelm and Battino (*8*).

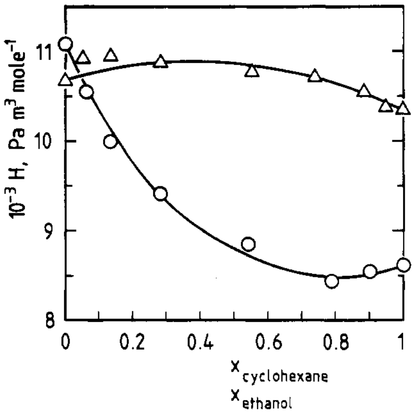

**Figure 1.** Henry's constants for oxygen in mixtures of cyclohexane and benzene (○) and ethanol and toluene (△) at 293.2 K (—, eq 2).

Henry's constants in the pure liquids are compared to the available literature data (*1*, *8*) in Table IV. The deviations are nonsystematic and amount to an average of 7%. (The oxygen solubilities in aniline and ethyl acetate reported by Schläpfer et al. (*5*) deviate by +69% and −30%, respectively, and are not considered.) Solubility data for $CO_2$ were available not for the temperature of 293.2 K but for 298.15 K. The mean deviation of 9.2% is therefore systematic, but it is still small as compared to the errors of the two models listed in Table IV. The strong specific interactions of $CO_2$ with the liquids are obviously not sufficiently accounted for. For most gases the regular-solution theory (*6*) agrees better with the observations than the scaled-particle theory (*7*). However, one has to consider that the comparison is not for the same gas/liquid systems: a major

**Table V. Effect of the Lennard-Jones Parameters for the Gas on the Description of the Measured Oxygen Solubilities by the Scaled-Particle Theory**

| $10^{10}\sigma$, m | $\epsilon/k$, K | source | mean devn, % |
|---|---|---|---|
| 3.460 | 118.0 | ref *9* | 52.7 |
| 3.467 | 106.7 | ref *10* | 18.8 |
| 2.902 | 73.4 | optimization | 2.2 |

advantage of the scaled-particle theory is its applicability to polar solvents.

In the case of hydrogen, the predictions of the scaled-particle theory are very close to the experimental results. It was tried to get a better fit also for oxygen by modification of the gas-specific Lennard-Jones parameters (Table V). If the parameters of Hirschfelder et al. (*9*) used by Battino and Wilhelm (*7*) are substituted by those suggested by Reid et al. (*10*), the mean error of the estimated oxygen solubilities is reduced from 52.7% to 18.8%. Fitting the two parameters to the experimental data but still using the same liquid-specific parameters, the mean error is only 2.2%. This is already close to the experimental error. It is therefore considered to empirically modify the scaled-particle theory by fitting also the gas-specific parameters to a larger set of experimental gas solubilities.

## Acknowledgment

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## Glossary

| | |
|---|---|
| $H$ | Henry's constant, Pa m$^3$ mol$^{-1}$ |
| $k$ | Boltzmann constant, J K$^{-1}$ |
| $\Delta P$ | pressure change by absorption, Pa |
| $P_0$ | barometric pressure, Pa |
| $P_L$ | vapor pressure of liquid, Pa |
| $R$ | gas constant, J K$^{-1}$ mol$^{-1}$ |
| $T$ | temperature, K |
| $V_{G(L)}$ | gas (liquid) volume, m$^3$ |
| $x_{1(2)}$ | mole fraction of component 1 (2) in binary mixtures |

*Greek Letters*

| | |
|---|---|
| $\alpha_{1,2}$ | expansion factor (eq 2) |
| $\epsilon$ | Lennard-Jones energy, J K$^{-1}$ |
| $\sigma$ | Lennard-Jones distance, m |

**Registry No.** H, 1333-74-0; He, 7440-59-7; N, 7727-37-9; CO, 630-08-0; O, 7782-44-7; $CO_2$, 124-38-9; acetone, 67-64-1; aniline, 62-53-3; benzene, 71-43-2; 1-butanol, 71-36-3; *n*-butyl acetate, 123-86-4; carbon tetrachloride, 56-23-5; cyclohexane, 110-82-7; decalin, 91-17-8; 1,2-dichloroethane, 107-06-2; 1,4-dioxane, 123-91-1; ethanol, 64-17-5; ethyl acetate, 141-78-6; ethylbenzene, 100-41-4; methanol, 67-56-1; nitrobenzene, 98-95-3; 2-propanol, 67-63-0; 1-tetradecene, 1120-36-1; tetralin, 119-64-2; 1,2,4-trimethylbenzene, 95-63-6; toluene, 108-88-3; *m*-xylene, 108-38-3.

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# Representation of Vapor-Liquid Equilibrium Data for Binary Refrigerant Mixtures

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**Vapor-liquid measurements were performed on binary refrigerant mixtures by using a Jones circulation unit with circulated vapor phase. Results from the equilibrium measurements on the binary refrigerants $CCl_2F_2/C_2Cl_2F_4$, $CHClF_2/C_2Cl_2F_4$, and $CHClF_2/CCl_2F_2$ in the pressure range 3.50-14.50 bar are presented. Comparisons were made between experimental equilibrium data and theoretically calculated data based on the following equations of state: Soave-Redlich-Kwong, de Santis, and Lee-Kesler-Plöcker. Good agreement was obtained between the modified Redlich-Kwong equation of state by Soave and the Lee-Kesler-Plöcker equation of state. In some cases and within small concentration intervals, the de Santis equation of state was found to give divergences. This may be explained by the uncertainty in the temperature-dependent parameters determined from pressure-volume-temperature data at temperatures near the critical.**

## Introduction

It is necessary to have relevant experimental data in order to make a comparison possible between different theoretical models that describe vapor-liquid equilibrium properties. An area of increasing interest is that of binary systems of refrigerant mixtures. However, such data have been published only to a very limited extent (*1*, *2*). In the present study isobaric measurements of vapor-liquid equilibrium data were performed for the three systems $CCl_2F_2/C_2Cl_2F_4$, $CHClF_2/C_2Cl_2F_4$, and $CHClF_2/CCl_2F_2$, in the pressure range 3.5-14.5 bar.

## Theory

The conditions for equilibrium between the vapor and the liquid phase can be expressed as

$$f_i^V = f_i^L \tag{1}$$

where $f_i^V$ is the fugacity of component $i$ in the vapor phase and $f_i^L$ is the fugacity of component $i$ in the liquid phase.

The fugacity of component $i$ in a mixture is related to the pressure $P$ and the composition $z_i$ by the fugacity coefficient according to

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