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Solubility of Gases in Liquids. 19. Solubility of He, Ne, Ar, Kr, Xe, N_2, O_2, CH_4, CF_4, and SF_6 in Normal 1-Alkanols n-$C_lH_{2l+1}OH$ ($1 \leq l \leq 11$) at 298.15 K†

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The Ostwald coefficients $L_{2,1}$ of He, Ne, Ar, Kr, Xe, N_2, O_2, CH_4, CF_4, and SF_6 dissolved in several homologous alkan-1-ols, n-$C_lH_{2l+1}OH$, $1 \leq l \leq 11$, have been determined at 298.15 K and atmospheric pressure. Altogether, 102 gas/liquid systems were investigated. The medium precision apparatus (about ±0.5%) was of the Ben-Naim/Baer type, similar to our recently published design. Data reduction is presented in some detail, including the estimation of auxiliary quantities, such as second virial coefficients and partial molar volumes at infinite dilution. The effect of chain length l is shown, and several correlations between $L_{2,1}$ (and/or the derived Henry fugacity $H_{2,1}$) and appropriate molecular and/or bulk properties of the gases and solvents are discussed.

Introduction

Data on the solubility of gases in liquids are of profound theoretical interest, and are reported in many application-oriented areas, including chemical process design, geochemistry, biomedical technology, and biophysics (*1–4*). While water is *the* ubiquitous and most important of all liquids, it is also the most complex, owing to the possibility of its molecules to form a three-dimensional hydrogen-bonded network structure (*2, 5, 6*). Normal 1-alkanols belong to a simpler class of hydrogen-bonded liquids, in that the aggregates formed are chains and rings (*7*). This decisively different situation is, of course, reflected by the observed differences of the thermodynamic properties associated with the dissolution of simple nonpolar solutes either in water or in 1-alkanols (*1, 2, 8–10*). In fact, solubilities of gases in alcohols have received particular attention in connection with studies of membranes, of the mechanism of general anesthesia, and so forth, not the least because of the use of the experimental 1-octanol/water partition coefficients for correlating anesthetic potency (*11–18*). 1-Octanol/water was chosen as the standard reference system for reasons connected with the ease of obtaining pure normal 1-octanol, its intermediate degree of polarity, and its reasonably long aliphatic chain. The influence of chain length upon solubility and in particular the investigation of even–odd effects, if any, are closely related problems. However, solubility data of gases dissolved in 1-alkanols are scattered throughout the literature and refer predominantly to short-chain members of the series. In addition, noticeable differences between published values are not uncommon. Against this background it seemed desirable and timely to embark on a reasonably comprehensive study of the solubility of gases in a series of normal 1-alkanols. Thus, we present here Ostwald coefficients $L_{2,1}$, and derived Henry fugacities $H_{2,1}$, of the 10 gases He, Ne, Ar, Kr, Xe, N_2, O_2, CH_4, CF_4, and SF_6 in normal 1-alkanols, n-$C_lH_{2l+1}OH$ with $1 \leq l \leq 11$ at 298.15 K. Altogether, data on 102 liquid/gas systems are reported. The temperature dependence of the solubilities will be investigated in a future project.

For the solubility measurements, a flow equilibration method was used. The instrument is similar to the Ben-Naim/Baer-type apparatus (*19*) recently presented by us (*20*), though without the microprocessor for pressure control and measurement of gas volume. It is for medium-precision work with an imprecision not exceeding ±1%. The measured Ostwald coefficients are converted to Henry fugacities by using the thermodynamically rigorous relations given by Wilhelm (*3, 4, 21–23*).

Experimental Section

The normal 1-alkanols used in this work were from several sources. Ethanol was from Pharmco (USP 200 proof), 1-hexanol was Eastman "practical" grade, and methanol, 1-propanol, 1-butanol, 1-pentanol, 1-heptanol, and 1-octanol were Fisher "certified" grade. 1-Nonanol, 1-decanol, and 1-undecanol were from Fluka. All the solvents were distilled at least once through a 1.2-m vacuum-jacketed packed column at a reflux ratio of 15 or better, and only the middle 80% of the distillate was used for the solubility measurements. The refractive indices of the pure alcohols were in good agreement with reliable literature values. Some of the distilled solvents were checked for purity by gas chromatography with the following results: 1-propanol, 99.8%; 1-pentanol, 99.3%, 1-hexanol, 99.6%; 1-heptanol, 99.6%; 1-octanol, 99.2%. The solvents were stored in brown glass bottles. Prior to actual solubility measurements they were degassed by the method of Battino et al. (*24*) and transferred under their own vapor pressure into the apparatus.

All gases were used from the gas tanks as received. They were from Matheson or Airco and had the following minimum mole percentage purities: He, 99.999; Ne, 99.994; Ar 99.9995; Kr, 99.9; Xe, 99.995; N_2, 99.999; O_2, 99.95; CH_4, 99.99; CF_4, 99.7; SF_6, 99.8.

The solubility apparatus was housed in a large air thermostat, the temperature of which was controlled to better than ±0.1 K with a Yellow Springs Instrument Co. Model 72 proportional controller. Temperatures T are based on IPTS-68, and were determined with a Leeds and Northrup knife blade platinum resistance thermometer, which was calibrated with a triple-point-of-water cell and an NBS-certified benzoic acid cell.

We used a Ben-Naim/Baer-type apparatus similar to that described in detail in ref 20. Depending on the magnitude

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of the Ostwald coefficient, four equilibration chambers with volumes of approximately 26, 65, 380, and 1650 cm^3 can be used. The equilibration vessels and the gas burets were calibrated with doubly distilled water, and the respective volumes are known to better than ±0.01 cm^3. The total pressure P was determined with a C. J. Enterprise Model CJCD-3091L pressure transducer.

The imprecision of our measurements was found to be about ±1% for the xenon solutions (they have the largest Ostwald coefficients), about ±0.8% for the systems with helium and neon (very small solubilities), and ±0.5% or better for all the other systems. The inaccuracy of this type of instrument was shown to be of the same order of magnitude (*20*), which was further corroborated by test measurements of $L_{2,1}$ of oxygen dissolved in water at 298.15 K and atmospheric pressure, which yielded results to within ±0.5% of the best literature values (*21*, *25*).

Data Reduction

The Ostwald coefficient is a convenient and frequently used measure of the solubility of a gas in a liquid. Of the several definitions of the Ostwald coefficient introduced in the literature (*26*), the most appropriate one for a thermodynamically rigorous description of gas solubility is (*3*, *4*, *20–23*)

$$L_{2,1}(T,P) = (c_2^{\mathrm{L}}/c_2^{\mathrm{V}})_{\mathrm{equil}} \qquad (1)$$

Here $c_2^{\mathrm{L}} = x_2/V^{\mathrm{L}}$ and $c_2^{\mathrm{V}} = y_2/V^{\mathrm{V}}$ are the amount-of-substance concentrations, at $\{T, P\}$, of the solute (gas) in the liquid-phase solution (indicated by a superscript L) and in the coexisting vapor-phase solution (indicated by a superscript V), respectively. The mole fraction of gas in the liquid phase is x_2, y_2 is the mole fraction of gas in the vapor phase, and V^{L} and V^{V} are the corresponding molar volumes. The link with the experimentally accessible quantities is established through

$$L_{2,1}(T,P) = v^{\mathrm{V}}/v^{\mathrm{L}} \qquad (2)$$

where v^{V} is the volume determined with the gas burets and v^{L} is the volume of the liquid solution after equilibrium is reached.

As indicated, $L_{2,1}(T,P)$ depends on temperature as well as on total pressure. However, for conditions well below the critical point of the solvent, the pressure dependence is usually very small and can be detected only by measurement techniques of the highest accuracy, that is to say by methods where the experimental error is, roughly, less than 0.1% (see refs 21 and 27–29). Thus, given the limits of experimental precision attainable with this apparatus, to an excellent approximation the Henry fugacity $H_{2,1}(T,P_{s,1})$ is given by (*3*, *4*, *20–23*)

$$H_{2,1}(T,P_{s,1}) = RTZ^{\mathrm{V}}\phi_2^{\mathrm{V}}I_2^{-1}/(V^{\mathrm{L}}L_{2,1}(T,P)) \qquad (3)$$

where the Poynting term is

$$I_2 = \exp[\int_{P_{s,1}}^{P}(RT)^{-1}V_2^{\mathrm{L}}\,\mathrm{d}P]$$
$$\simeq \exp[(RT)^{-1}V_2^{\mathrm{L}\infty}(P-P_{s,1})] \qquad (4)$$

Here, $Z^{\mathrm{V}} = PV^{\mathrm{V}}/RT$ is the vapor-phase compressibility factor, ϕ_2^{V} is the vapor-phase fugacity coefficient of the solute, $P_{s,1}$ is the vapor pressure of pure solvent, and R is the gas constant. As concerns the liquid phase, V^{L} is the corresponding molar volume, V_2^{L} is the partial molar volume of dissolved gas at mole fraction x_2, and $V_2^{\mathrm{L}\infty}$ is the partial molar volume of the gas at infinite dilution.

Table I. Vapor Pressures $P_{s,1}$, Densities $\rho_1^{\mathrm{L}*}$, Isobaric Expansivities $\alpha_{P,1}^{\mathrm{L}*}$, Isothermal Compressibilities $\beta_{T,1}^{\mathrm{L}*}$, and Internal Pressures $\Pi_1^{\mathrm{L}*}$ of Normal 1-Alkanols n-$C_lH_{2l+1}OH$ at T = 298.15 K

alcohol	$P_{s,1}$/Pa^a	$10^{-3}\rho_1^{\mathrm{L}*}$/(kg·m^{-3})	$10^3\alpha_{P,1}^{\mathrm{L}*}$/K^{-1}	$10^{12}\beta_{T,1}^{\mathrm{L}*\,d}$/Pa^{-1}	$10^{-6}\Pi_1^{\mathrm{L}*\,e}$/Pa
methanol	16941	0.7866^b	1.195^b	1248	285
ethanol	7876	0.7851^b	1.093^b	1153	281
1-propanol	2786	0.7996^b	0.995^b	1006	295
1-butanol	858	0.8058^b	0.932^b	942	295
1-pentanol	259	0.8111^b	0.893^b	884	301
1-hexanol	77	0.8154^b	0.870^b	836	310
1-heptanol	22	0.8194^c	0.861^c	800	321
1-octanol	6	0.8218^b	0.854^c	777	328
1-nonanol	2	0.8245^c	0.826^c	752	327
1-decanol	<1	0.8266^b	0.812^c	733	330
1-undecanol	<1	0.8292^c	0.813^c	723	335

[a] Reference 30. [b] Reference 31. [c] Derived from densities reported in ref 32 via polynomial smoothing: $\rho_1^{\mathrm{L}*} = A_0 + A_1T + A_2T^2$. [d] Reference 32. [e] Calculated from eq 18.

For gas solubility measurements at such low pressures as in this work, the virial equation in pressure in the truncated form

$$Z^{\mathrm{V}} = 1 + (RT)^{-1}P(y_1B_{11} + y_2B_{22} + y_1y_2\Delta_{12}) \qquad (5)$$

is adequate for the description of real-gas behavior; hence

$$\phi_i^{\mathrm{V}} = \exp[(RT)^{-1}P(B_{ii} + y_j^2\Delta_{12})], \quad i, j = 1,2, \quad i \neq j \qquad (6)$$

B_{11} and B_{22} are the second virial coefficients of pure solvent vapor and gas, respectively, B_{12} is the second virial cross-coefficient, and $\Delta_{12} = 2B_{12} - (B_{11} + B_{22})$. The molar volume of the liquid solution is obtained from the asymptotically valid expression

$$V^{\mathrm{L}} = x_1V_{s,1}^{\mathrm{L}*} + x_2V_2^{\mathrm{L}\infty} \qquad (7)$$

where $V_{s,1}^{\mathrm{L}*}$ is the molar volume of pure liquid solvent at saturation conditions. At the level of approximation indicated by eq 3, the liquid-phase mole fraction is given by

$$x_2 = P_2V^{\mathrm{L}}L_{2,1}(T,P)/(RTZ^{\mathrm{V}}) \qquad (8)$$

where $P_2 = y_2P$ is the partial pressure of the gas. For computational details of the rapidly converging iteration procedure used to calculate the mole fractions, the fugacity coefficients, etc., see refs 20 and 21.

The vapor pressures of the alcohols and their densities were taken from refs 30–32 (see Table I). Relative atomic masses were taken from the table published by IUPAC in 1986 (*33*). The auxiliary quantities necessary for calculating $H_{2,1}(T,P_{s,1})$, that is to say the virial coefficients and $V_2^{\mathrm{L}\infty}$, were either obtained from the literature or estimated as follows.

Virial Coefficients. Virial coefficients B_{22} of the pure gases were taken from Dymond and Smith (*34*); virial coefficients B_{11} of the pure solent vapors were estimated using the Tsonopoulos correlation (*35–38*)

$$B_{ii}P_{c,i}/(RT_{c,i}) = B^{(0)}(T_{r,i}) + \omega_iB^{(1)}(T_{r,i}) + B^{(2)}(T_{r,i}) \qquad (9)$$

$B^{(0)}(T_{r,i})$ and $B^{(1)}(T_{r,i})$ are universal functions of the reduced temperature $T_{r,i} = T/T_{c,i}$, $P_{c,i}$ and $T_{c,i}$ are the critical pressure and the critical temperature of pure i, respectively, and ω_i is the acentric factor. The polar contribution $B^{(2)}(T_{r,i})$ is given by

$$B^{(2)}(T_{r,i}) = a/T_{r,i}^{\,6} - b/T_{r,i}^{\,8} \qquad (10)$$

It is zero for nonpolar (or slightly polar) substances. For non-hydrogen-bonded polar compounds $b = 0$, and a depends on the compound class. For the hydrogen-bonded normal 1-alkanols, Tsonopoulos set $a = 0.0878$, while b appears to be

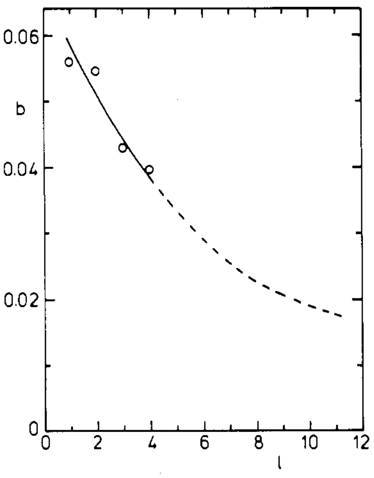

Figure 1. Correlation of parameter b of the polar contribution $B^{(2)}(T_{r,i})$ to the second virial coefficient of normal 1-alkanols (see eq 10) with chain length l of n-$C_lH_{2l+1}OH$. The circles represent optimized values for methanol, ethanol, 1-propanol, and 1-butanol, respectively (see text). The parameter a = 0.0878.

a function of the reduced dipole moment (*39*)

$$\mu_{r,i}^2 = \mu_i^2 N_A/(4\pi\epsilon_0 V_{c,i} k_B T_{c,i}) \qquad (11)$$

though this dependence still needs quantification by data on the higher 1-alkanols. Here, μ_i is the permanent electric dipole moment of substance i, $V_{c,i}$ is its critical molar volume, ϵ_0 is the permittivity of a vacuum, N_A is the Avogadro constant, and k_B is the Boltzmann constant.

Using the most reliable data on the second virial coefficients B_{11} of methanol, ethanol, 1-propanol, and 1-butanol (*38*), b values were evaluated so as to yield optimum agreement, in the temperature range up to 420 K, between these experimental results and B_{11} calculated via eqs 9 and 10. Figure 1 shows a plot of b vs chain length l. The extrapolated, dashed part of the curve should not be given undue significance; it merely guarantees a physically reasonable increase with chain length of the polar contribution $B^{(2)}(T_{r,i})$. The critical quantities of the pure normal 1-alkanols (i = 1) were taken from Teja et al. (*40*), and their acentric factors were taken from Ambrose and Walton (*41*) (see Table II).

For the estimation of virial cross-coefficients B_{12}, it is assumed that the same relations (eqs 9 and 10) hold, but with characteristic parameters $T_{c,12}$, $P_{c,12}$, and ω_{12} replacing the corresponding pure-substance quantities (*38*, *42*). Thus, reduced virial cross-coefficients $B_{12}(T_r)P_{c,12}/(RT_{c,12})$ are obtained at a reduced temperature $T_r = T/T_{c,12}$, with

$$T_{c,12} = (1 - k_{12})(T_{c,1}T_{c,2})^{1/2} \qquad (12)$$

$$P_{c,12} = Z_{c,12}RT_{c,12}/V_{c,12} \qquad (13)$$

$$V_{c,12} = 0.125(V_{c,1}^{1/3} + V_{c,2}^{1/3})^3 \qquad (14)$$

$$Z_{c,12} = (Z_{c,1} + Z_{c,2})/2 \qquad (15)$$

$$\omega_{12} = (\omega_1 + \omega_2)/2 \qquad (16)$$

For polar/nonpolar binaries, B_{12} is assumed to have no polar term; that is, $a_{12} = 0$ and $b_{12} = 0$. The critical quantities $T_{c,2}$, $P_{c,2}$, and $V_{c,2}$ of the pure gases, as well as their acentric factors ω_2, were taken from Reid et al. (*43*). The binary interaction parameter k_{12} is a characteristic constant for each binary.

The most sensitive mixing rule is eq 12, and k_{12} may be estimated by various semiempirical correlations (*20*, *38*, *42*). For the present purpose, we adopted the suggestion of Tsonopoulos et al. and correlated k_{12} with $V_{c,2}$ for the systems up to l = 5 as shown in Figure 2, which is based on an analysis of all relevant experimental data (*38*, *42*). For $l \geq 6$, k_{12} was set equal to an average value of 0.27.

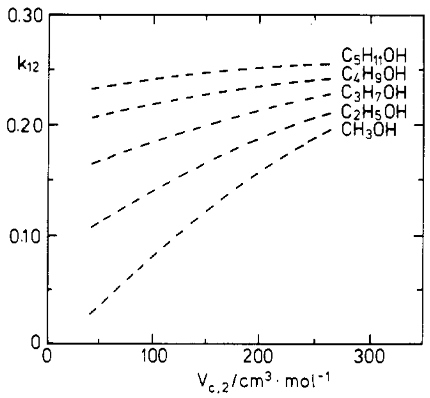

Figure 2. Correlation of the binary interaction parameter k_{12} (see eq 12) for 1-alkanol/nonpolar binaries ($l \leq 5$) with the critical volume $V_{c,2}$ of the nonpolar component. This plot is based on the optimum k_{12} values presented by Tsonopoulos (*38*, *42*).

Table II. Acentric Factors ω_1 (41), Critical Temepratures $T_{c,1}$, Critical Pressures $P_{c,1}$, and Critical Molar Volues $V_{c,1}$ (40) of Normal 1-Alkanols n-$C_lH_{2l+1}OH$

alcohol	ω_1	$T_{c,1}$/K	$10^{-6}P_{c,1}$/Pa	$10^6V_{c,1}/(m^3 \cdot mol^{-1})$
methanol	0.564	512.6	8.092	117.8
ethanol	0.643	514.1	6.140	166.9
1-propanol	0.620	536.7	5.168	218.5
1-butanol	0.591	562.4	4.418	274.5
1-pentanol	0.579	588.0	3.868	326.5
1-hexanol	0.575	611.0	3.413	393.0
1-heptanol	0.580	632.5	3.058	435.2
1-octanol	0.594	652.6	2.777	506.7
1-nonanol	0.610	670.5	2.546	572.4
1-decanol	0.629	687.1	2.320	648.7
1-undecanol	0.656	703.3	2.147	718.0

Partial Molar Volumes. Experimental partial molar volumes at infinite dilution, $V_2^{L\infty}$, have been reported for quite a number of 1-alkanol/gas systems (*44*–*46*). They are well represented, i.e., usually to within 10%, by

$$V_2^{L\infty}P_{c,2}/RT_{c,2} = 0.088 + 2.763TP_{c,2}/(T_{c,2}\Pi_1^{L*}) \qquad (17)$$

where $\Pi_1^{L*} = (\partial U_1^{L*}/\partial V)_T$ is the internal pressure and U_1^{L*} is the internal energy of the pure solvent. The internal pressure was calculated according to the thermodynamic relation

$$\Pi_1^{L*} = T\alpha_{P,1}^{L*}/\beta_{T,1}^{L*} - P \qquad (18)$$

where $\alpha_{P,1}^{L*}$ is the isobaric expansivity and $\beta_{T,1}^{L*}$ is the isothermal compressibility of the pure alcohol (*31*, *32*). These quantities have been included in Table I. In this work, all partial molar volumes at infinite dilution were calculated via eq 17.

Results and Discussion

Experimental Ostwald coefficients $L_{2,1}(T,P)$ at T = 298.15 K and P = 101 325 Pa are given in Table III, together with the Henry fugacities $H_{2,1}(T,P_{s,1})$ calculated from eq 3, and the mole fraction solubilities x_2 at P_2 = 101 325 Pa calculated from eq 8. Agreement with reliable literature values (*1*, *15*, *17*, *47*–*59*) is in general quite satisfactory. By way of example, such a comparison is presented in Table IV for the three solutes xenon, nitrogen, and methane dissolved in normal 1-alkanols n-$C_lH_{2l+1}OH$, $1 \leq l \leq 10$, at 298.15 K and 101 325 Pa. We note, however, that for xenon the recent results of Prorokov, Dolotov, and Krestov (*60*) appear to be much too

Table III. Ostwald Coefficients $L_{2,1}(T,P)$ of 10 Gases Dissolved in Normal 1-Alkanols n-$C_lH_{2l+1}OH$, $1 \le l \le 11$, at T = 298.15 K and P = 101 325 Pa and Henry Fugacities $H_{2,1}(T,P_{s,1})$ and Mole Fraction Solubilities x_2 at a Partial Pressure P_2 = 101 325 Pa at the Same Temperature

gas	$L_{2,1}(T,P)$	$10^{-6}H_{2,1}(T,P_{s,1})$/Pa	10^4x_2	$L_{2,1}(T,P)$	$10^{-6}H_{2,1}(T,P_{s,1})$/Pa	10^4x_2	$L_{2,1}(T,P)$	$10^{-6}H_{2,1}(T,P_{s,1})$/Pa	10^4x_2
		Methanol			Ethanol			1-Propanol	
He	0.03450	1764	0.575	0.03030	1394	0.727	0.02766	1192	0.849
Ne	0.04732	1285	0.789	0.04320	977.5	1.036	0.03833	860.2	1.177
Ar				0.2634	159.9	6.327	0.2459	133.7	7.558
Kr	0.6407	94.28	10.73	0.6879	61.02	16.55	0.6929	47.33	21.32
Xe							2.376	13.72	73.30
N_2	0.1536	395.0	2.566	0.1460	288.6	3.506	0.1327	248.0	4.078
O_2				0.2412	174.6	5.794	0.2193	150.0	6.741
CH_4	0.5022	120.4	8.404	0.5074	82.77	12.20	0.5150	63.71	15.85
CF_4	0.1855	324.5	3.110	0.1917	218.1	4.620	0.1731	188.6	5.338
SF_6	0.6178	95.86	10.44	0.7505	54.78	18.24	0.7377	43.53	22.94
		1-Butanol			1-Pentanol			1-Hexanol	
He	0.02571	1048	0.966	0.02321	982.2	1.030	0.02147	921.0	1.099
Ne	0.03520	765.3	1.323	0.03228	706.4	1.433	0.02999	659.4	1.535
Ar	0.2404	111.8	9.041	0.2270	100.2	10.08	0.2177	90.66	11.15
Kr	0.6725	39.87	25.31	0.6453	35.18	28.68	0.6313	31.20	32.34
Xe	2.554	10.45	96.21	2.428	9.32	107.9	2.416	8.13	123.6
N_2	0.1222	220.0	4.595	0.1154	197.2	5.126	0.1110	177.9	5.684
O_2	0.2119	126.8	7.970	0.1982	114.8	8.806	0.1904	103.6	9.752
CH_4	0.4923	54.47	18.53	0.4711	48.20	20.94	0.4514	43.64	23.13
CF_4	0.1580	168.9	5.962	0.1401	161.2	6.245	0.1303	150.4	6.696
SF_6	0.6775	38.75	25.76	0.6180	35.97	27.75	0.5624	34.29	29.11
		1-Heptanol			1-Octanol			1-Nonanol	
He	0.01968	887.8	1.140	0.08190	827.3	1.224	0.01808	783.3	1.292
Ne	0.02865	610.0	1.660	0.02689	581.6	1.741	0.2544	556.8	1.818
Ar	0.2066	84.42	11.97	0.1990	78.44	12.89	0.1920	73.64	13.73
Kr	0.6036	28.85	34.98	0.5813	26.82	37.63	0.5806	24.33	41.48
Xe	2.388	7.28	138.0						
N_2	0.1044	167.1	6.050	0.09485	164.6	6.142	0.09065	156.0	6.481
O_2	0.1798	96.99	10.42	0.1707	91.42	11.06	0.1658	85.27	11.85
CH_4	0.4438	39.23	25.73	0.4196	37.14	27.18	0.4089	34.53	29.23
CF_4	0.1218	142.2	7.083	0.1135	136.5	7.375	0.1079	130.1	7.741
SF_6	0.5366	31.77	31.42	0.5031	30.33	32.91	0.4812	28.73	34.75
		1-Decanol			1-Undecanol				
He	0.01785	725.0	1.396	0.01755	679.5	1.490			
Ne	0.02475	522.9	1.936	0.02307	517.0	1.958			
Ar	0.1872	69.02	14.64	0.1783	66.78	15.14			
Kr	0.5442	23.72	42.55	0.5322	22.36	45.14			
Xe									
N_2	0.08567	150.8	6.703	0.08529	139.6	7.242			
O_2	0.1580	81.76	12.36	0.1548	76.91	13.14			
CH_4	0.3909	33.01	30.58	0.3880	30.65	32.93			
CF_4	0.1014	126.5	7.961	0.09624	122.8	8.199			
SF_6	0.4527	27.91	35.77	0.4351	26.77	37.30			

Table IV. Comparison with Selected Literature Values: Ostwald Coefficients $L_{2,1}(T,P)$ of Xenon, Nitrogen, and Methane Dissolved in Normal 1-Alkanols n-$C_lH_{2l+1}OH$, $1 \le l \le 10$, at T = 298.15 K and P = 101 325 Pa

	$L_{2,1}(T,P)$					
	Xe		N_2		CH_4	
alcohol	this work	lit.	this work	lit.	this work	lit.
methanol		2.09,[a] 1.40[b]	0.1536	0.1645 (48), 0.167 (51), 0.140,[c] 0.164 (54)	0.5022	0.523 (50), 0.552 (51), 0.5180 (52)
ethanol		2.31,[a] 1.77[b]	0.1460	0.1489 (48), 0.149 (51), 0.152,[c] 0.149 (54), 0.1494 (55)	0.5074	0.534 (50), 0.539 (51), 0.5272 (52)
1-propanol	2.376	2.51,[a] 2.26[b]	0.1327	0.132 (49), 0.133 (51), 0.125,[c] 0.131 (54), 0.1313 (56)	0.5150	0.510 (51), 0.5090 (52)
1-butanol	2.554	2.54,[a] 2.27[b]	0.1222	0.1225 (48), 0.122 (51), 0.123 (54)	0.4923	0.509 (51), 0.4898 (52)
1-pentanol	2.428	2.49[a]	0.1154	0.111 (49), 0.116 (51)	0.4711	0.483 (51), 0.4676 (52)
1-hexanol	2.416	2.47[a]	0.1110	0.114 (51)	0.4514	0.464 (51), 0.4463 (52)
1-heptanol	2.388	2.44[a]	0.1044	0.105 (51)	0.4438	0.448 (51)
1-octanol		2.38[a]	0.09485	0.102 (51), 0.0963 (15)	0.4196	0.436 (51), 0.415 (15)
1-decanol		2.32[a]	0.08567	0.0854 (15)	0.3909	0.405 (15)

[a] Reference 17, interpolated. [b] Calculated from data given in ref 60. [c] Reference 53, interpolated.

low (a similar comment applies to the argon and krypton solubilities reported by these researchers). Figure 3 shows the Ostwald coefficients at 298.15 K of He, Ne, Ar, N_2, O_2, and CF_4 dissolved in n-$C_lH_{2l+1}OH$ as a function of chain length l, and Figure 4 shows such a plot for Kr, Xe, CH_4, and SF_6. A few supplementary results from the literature (*17, 48, 61*)—so as to have a complete set of data points for $1 \le l \le 11$—have been included (they are indicated by filled circles). The existence of *maxima* at small values of l for some series is particularly noteworthy: the maxima become more prominent the larger the solute and/or the solute's solubility. However, no extrema are observed for plots $H_{2,1}$ vs l and x_2 vs l.

Scaled particle theory (SPT) has been used successfully for the prediction and correlation of Henry fugacities (*2–4, 23, 62–69*). For the suggested two-step dissolution process

$$\ln(H_{2,1}V_{s,1}^{L^*}/RT) = G_{CAV}/RT + G_{INT}/RT \qquad (19)$$

where G_{CAV} is the partial molar Gibbs energy of cavity

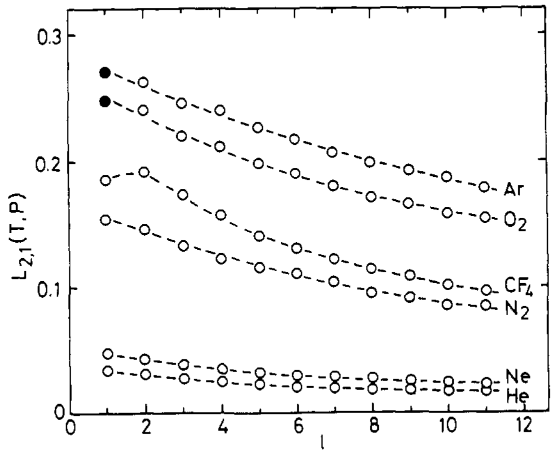

Figure 3. Ostwald coefficients $L_{2,1}(T,P)$ of He, Ne, Ar, N_2, O_2, and CF_4 dissolved in normal 1-alkanols $n\text{-}C_lH_{2l+1}OH$ as a function of chain length l for $T = 298.15$ K, $P = 101\,325$ Pa, and $1 \leq l \leq 11$: (○) experimental results of this work; (●) experimental results from the literature (Ar, ref 61; O_2, ref 48). The broken curves are only meant to indicate the general trends.

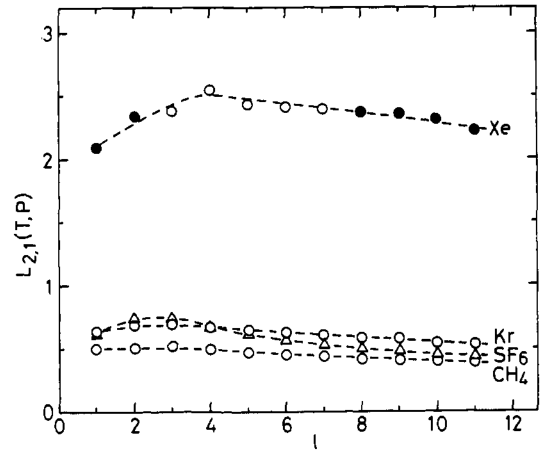

Figure 4. Ostwald coefficients $L_{2,1}(T,P)$ of Kr, Xe, CH_4, and SF_6 dissolved in normal 1-alkanols $n\text{-}C_lH_{2l+1}OH$ as a function of chain length l for $T = 298.15$ K, $P = 101\,325$ Pa, and $1 \leq l \leq 11$: (○, △) experimental results of this work; (●) experimental results from the literature (Xe, ref 17). The broken curves are only meant to indicate the general trends.

formation and G_{INT} is the partial molar Gibbs energy of interaction. SPT provides a reasonable approximation of G_{CAV} in that it yields an asymptotic expansion in the radius of the (spherical) cavity to be created in a solvent of *compactness* $N_A\sigma_1^3\pi/(6V_{s,1}^{L*})$, where σ_1 is the effective hard sphere diameter of the solvent (*66, 67, 70*). The interactional contribution G_{INT} may, as usual, be approximated by an effective Lennard-Jones term augmented by a term representing dipole–induced dipole interactions (*2, 3, 63–65, 68, 69*). Although SPT was developed for vastly different types of solutions, it works surprisingly well for the prediction of Henry fugacities (and related quantities) of gases in liquid alcohols and even water (*2–4, 15, 21, 27–29, 64, 68, 71*). By way of example, Table V shows a comparison between experimental and calculated $H_{2,1}$ of the 10 gases dissolved in ethanol at 298.15 K. The necessary effective molecular parameters were taken from Wilhelm and Battino (*66*). For the other alcohols, results are of similar quality. Considering the simplicity of the prediction method, the agreement is quite satisfactory.

Finally, the dependence of $P_{c,2}/H_{2,1}$ on the characteristic solvent size parameter $(V_{c,1}/N_A)^{1/3}$ is shown in Figure 5 for Kr, N_2, CH_4, and SF_6 dissolved in $n\text{-}C_lH_{2l+1}OH$; a similar pattern is observed for the other gases as well. The slightly curved graphs are well suited for estimating solubilities, that is, for interpolation and extrapolation to higher alcohols.

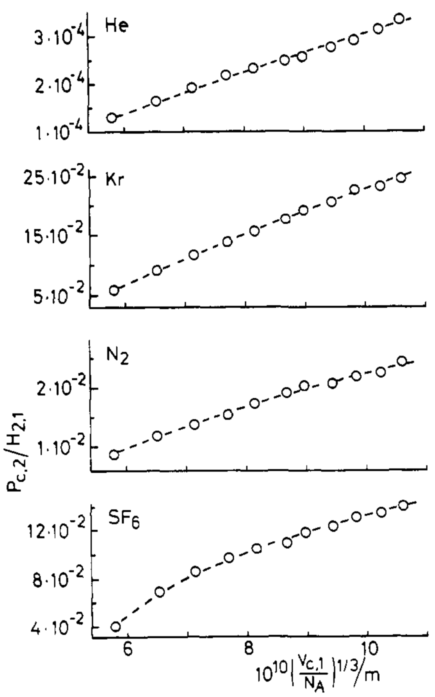

Figure 5. Correlation of the reduced reciprocal Henry fugacity $P_{c,2}/H_{2,1}$ of He, Kr, N_2, and SF_6 dissolved in normal 1-alkanols $n\text{-}C_lH_{2l+1}OH$ with the solvent size parameter $(V_{c,1}/N_A)^{1/3}$ at $T = 298.15$ K and for $1 \leq l \leq 11$: (○) experimental results of this work. The broken curves are only meant to indicate the general trends.

Table V. Comparison of Experimental Values of Henry Fugacities $H_{2,1}(T,P_{s,1})$ for 10 Gases Dissolved in Ethanol at $T = 298.15$ K with Results from the Scaled Particle Theory (SPT)

	$\ln[H_{2,1}(T,P_{s,1})/Pa]$			$\ln[H_{2,1}(T,P_{s,1})/Pa]$	
gas	exptl	SPT	gas	exptl	SPT
He	21.055	20.705	N_2	19.481	19.395
Ne	20.701	19.870	O_2	18.978	18.722
Ar	18.890	18.601	CH_4	18.232	18.099
Kr	17.927	18.044	CF_4	19.200	19.160
Xe	16.695	16.889	SF_6	17.819	17.528

Glossary

a,b	parameters of eq 10
$B^{(0)},B^{(1)},B^{(2)}$	Tsonopoulos functions (eq 9)
B_{ii}	second virial coefficient of pure i
B_{ij}	second virial cross-coefficient
c_2	amount-of-substance concentration of solute 2
G_{CAV}	partial molar Gibbs energy of cavity formation
G_{INT}	partial molar Gibbs energy of interaction
$H_{2,1}$	Henry fugacity of solute 2 dissolved in solvent 1
k_B	$=R/N_A = 1.380\,66 \times 10^{-23}$ J·K^{-1}, Boltzmann constant
k_{12}	binary interaction parameter
l	chain length of normal 1-alkanols, $n\text{-}C_lH_{2l+1}OH$
$L_{2,1}$	Ostwald coefficient of solute 2 dissolved in solvent 1
N_A	$=6.022\,045 \times 10^{23}$ mol^{-1}, Avogadro constant
P	pressure
P_2	$=y_2P$, partial pressure of solute 2
$P_{s,1}$	vapor pressure of solvent 1

I_2	Poynting correction
R	$=8.314\,41\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, gas constant
T	thermodynamic temperature
U_1^{L*}	internal energy of pure liquid solvent 1
v	experimentally determined volume
V^L	molar volume of a liquid solution
$V_{s,1}^{L*}$	molar volume of pure liquid 1 (saturation)
V_2^L	partial molar volume of solute 2 in the liquid phase
$V_2^{L\infty}$	partial molar volume of solute 2 in the liuqid phase at infinite dilution
x	liquid-phase mole fraction
y	vapor-phase mole fraction
Z	$=PV/RT$, compressibility factor

Greek Letters

$\alpha_{P,1}^{L*}$	isobaric expansivity of pure liquid solvent I
$\beta_{T,1}^{L*}$	isothermal compressibility of pure liquid solvent 1
Δ_{12}	$=2B_{12} - (B_{11} + B_{22})$
ϵ_0	$=8.854\,19 \times 10^{-12}\ \mathrm{F\cdot m^{-1}}$, permittivity of a vacuum
μ	electric dipole moment
Π_1^{L*}	internal pressure of pure liquid solvent 1
ρ_1^{L*}	density of pure liquid solvent 1
σ	effective hard sphere diameter
ϕ_i	fugacity coefficient of component i in solution
ω	acentric factor

Subscripts

c	critical (or pseudocritical) quantity
i	general index; frequently $i = 1$ denotes the solvent amd $i = 2$ the solute (gas)
ij	"binary" or "interaction" quantity
r	reduced quantity
s	saturation condition

Superscripts

*	pure substance
∞	infinite dilution
L	liquid phase
V	vapor phase

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