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Full Articles

Temperature dependence of the solubility of nitrogen in *n*-alkanes at atmospheric pressure

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The recently developed approach to the description of the solubility of noble gases and nitrogen in liquids was extended to the consideration of factors determining the temperature dependence of the solubility of these gases. The agreement of the theory and experiment was confirmed by the literature data on the solubility of nitrogen at a partial pressure of $1.01325 \cdot 10^5$ Pa in hexane, heptane, octane, decane, and hexadecane, which as a whole have a very wide (231—475 K) temperature range of validity. Henry´s constant is proved not to be the true characteristic of gas affinity to liquids. The thermodynamic parameters obtained on the basis of the temperature dependence of Henry´s constant are referred to the sum of two processes: the transfer of gas particles from the intrinsic phase to cavities of the intermolecular volume of the liquid and the change in the total volume of the cavities due to the thermal expansion (compression) of the liquid.

Key words: nitrogen, liquid *n*-alkanes, solubility, temperature dependence.

We have previously[1] shown that the solubility (in moles per mole of solvent) of noble gases and nitrogen in liquids can be described by the equation

$$n_2 = \frac{V_{\mathrm{l,m}}(k^* - k)}{(K_{\mathrm{D}}c_{\mathrm{g},\infty})^{-1} - V_{\mathrm{g},\infty}} = \frac{V_{\mathrm{l,m}}k^* - V_{\mathrm{l,W}}}{(K_{\mathrm{D}}c_{\mathrm{g},\infty})^{-1} - V_{\mathrm{g,W}}}. \qquad (1)$$

Here $V_{\mathrm{l,m}}$ is the molar volume of the liquid; k is the molecular packing coefficient of the liquid equal to the ratio of the intrinsic (van der Waals) volume of 1 mole of the liquid molecules ($V_{\mathrm{l,W}}$) calculated by the Askadskii method[2] to $V_{\mathrm{l,m}}$; k^* is the limiting value of this parameter corresponding to the condition $n_2 = 0$ and achieved at an external pressure characteristic of each liquid; $c_{\mathrm{g},\infty}$ is the equilibrium gas concentration in the intrinsic phase, mol m^{-3}; K_{D} is the size-independent gas partition constant of the *n*-alkane molecule between the intrinsic phase and its intermolecular volume ($V_{\mathrm{l,f}}^*$), which is accessible for diffusional migrations of gas particles that entered into the liquid; $V_{\mathrm{l,f}}^*$ is determined from the ratio

$$V_{\mathrm{l,f}}^* = V_{\mathrm{l,f}}(k^* - k) + n_2V_{\mathrm{g,W}}, \qquad (2)$$

where $V_{\mathrm{g,W}}$ is the van der Waals volume of 1 mole of gas molecules.

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It can easily be seen that K_D differs from the Ostwald absorption coefficient[3]

$$L = c_{g,\infty}/c_{g,S} \tag{3}$$

($c_{g,S}$ is the equilibrium gas concentration in the liquid per its physical volume unit) taking into account that the volume actually occupied by particles of the dissolved gas is substantially smaller than the physical volume of the liquid and the volume defined as the "free volume" and calculated as a difference between $V_{l,m}$ and $V_{l,W}$.

It is reasonable to assume that the k^* parameter is temperature-independent: only the pressure necessary for achieving this parameter should increase with the temperature increase. Therefore, under a constant gas pressure (P_g = const) the direction of change in n_2 with the temperature increase will depend on the sign of the temperature coefficient K_D and the ratio of absolute values of the temperature coefficients K_D, $V_{l,m}$, and $c_{g,\infty}$.

To illustrate this specific feature of the dissolution of simple gases in liquids, let us use the data available in literature[4—7] on the solubility of nitrogen in some n-alkanes at atmospheric pressure, which are referred, as a whole, to the very wide (213—475 K) temperature range.

Results and Discussion

The molar volumes of the considered n-alkanes were calculated taking into account their densities on the saturation line, and the equilibrium concentrations of nitrogen in the gas phase at 213—300 K were calculated on the basis of the specific volume under a pressure of 1 bar.[8] At $T > 300$ K nitrogen was considered to be an ideal gas. The intrinsic volumes of n-alkanes, the characteristic parameter $k^* = 0.626$, and the intrinsic volume of one mole of nitrogen $V_{g,W} = 13.9 \cdot 10^{-6}$ m^3 mol^{-1} are taken from Ref. 1.

The following conclusions can be drawn from an analysis of the calculation results listed in Table 1.

(1) In all cases considered, $V_{l,m}(k^* - k) >> n_2V_{g,W}$ and, therefore, the equation

$$K_D = n_2/[V_{l,m}(k^* - k)c_{g,\infty}]. \tag{4}$$

can be used for the calculation of K_D.

(2) In nitrogen—n-alkane system an increase in the solubility of the gas in the liquid with temperature is a result of a larger increment in $V_{l,f}^*$ compared to the reduction of K_D and $c_{g,\infty}$.

The K_D values calculated with allowance for nitrogen solubility values in all five n-alkanes (the exception is the K_D values in hexane at 213.15 K and in decane at 313.19 K) obey the same temperature dependence, forming (Fig. 1) a smooth curve in the coordinates $\ln K_D$—T

$$\ln K_D = 3.667 - 1.334 \cdot 10^{-2}T + 1.384 \cdot 10^{-5}T^2 \tag{5}$$

or grouping near one straight line in the coordinates $\ln K_D$—T^{-1}

$$\ln K_D = -0.4596 + 411.64T^{-1}. \tag{6}$$

However, although the K_D values calculated by these equations are close (see Table 1), the best agreement with experiment in the whole temperature range is given by the

Table 1. Temperature dependence of the solubility of nitrogen in n-alkanes at atmospheric pressure

Alkane	T/K	$V_{l,f}^*$	$n_2V_{g,W}$	$c_{g,\infty}$, /mol m^3	K_D			$n_2 \cdot 10^3$/mol mol^{-1}		
		10^{-6} m^3 mol^{-1}			Experiment	Calculation by Eq.		Experiment	Calculation by Eq.	
						(5)	(6)		(4), (5)	(4), (6)
Hexane	213.15	4.95	0.018	57.268	4.66	4.28	4.35	1.32	1.21	1.23
	233.15	6.66	0.018	52.336	3.71	3.71	3.69	1.30	1.29	1.29
	253.15	8.52	0.018	48.183	3.19	3.25	3.21	1.31	1.33	1.32
	273.15	10.52	0.019	44.638	2.85	2.88	2.85	1.34	1.35	1.34
	298.15	13.24	0.019	40.875	2.55	2.51	2.51	1.38	1.36	1.36
Heptane	308.15	14.07	0.019	39.561	2.46	2.39	2.40	1.37	1.33	1.34
Octane	308.05	13.89	0.019	39.561	2.44	2.39	2.40	1.34	1.31	1.32
Decane	283.18	10.44	0.017	43.054	2.71	2.72	2.70	1.22	1.22	1.21
	313.19	14.32	0.017	38.912	2.17	2.33	2.35	1.21	1.30	1.31
Hexadecane	300	12.28	0.018	40.623	2.55	2.49	2.49	1.27	1.24	1.24
	325	16.51	0.019	37.498	2.18	2.21	2.24	1.35	1.37	1.39
	350	20.98	0.020	34.819	1.96	2.00	2.05	1.43	1.46	1.50
	375	25.69	0.021	32.498	1.81	1.84	1.89	1.51	1.54	1.58
	400	30.76	0.023	30.467	1.73	1.73	1.77	1.62	1.62	1.66
	425	36.13	0.024	28.675	1.68	1.65	1.66	1.74	1.71	1.72
	450	41.92	0.025	27.082	1.61	1.60	1.58	1.83	1.82	1.79
	475	48.27	0.027	25.656	1.56	1.58	1.50	1.93	1.96	1.86

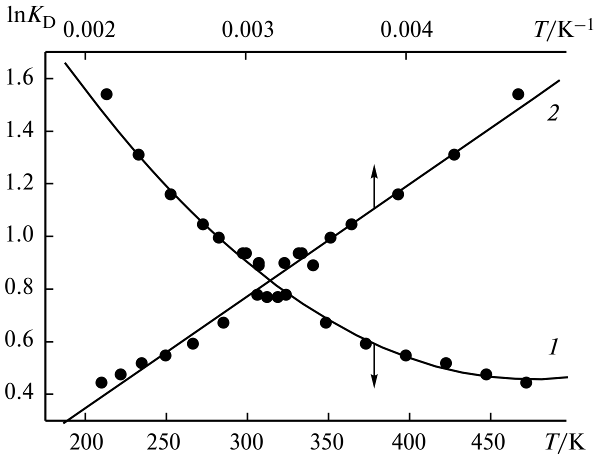

Fig. 1. Temperature dependence of the solubility of nitrogen in the coordinates $\ln K_D$—T (*1*) and $\ln K_D$—T^{-1} (*2*).

n_2 values calculated using the K_D values smoothened by Eq. (5).

Thus, Eq. (1) correctly reflects the temperature effect on the solubility of simple gases in liquids, while in the region of n_2 values corresponding to the partial gas pressure in the intrinsic phase $P_g \le 0.1$ MPa, it is validly to reduce Eq. (1) to the equation

$$n_2 = K_D c_{g,\infty} V_{1,m}(k^* - k). \qquad (7)$$

The signs of the temperature coefficients n_2 and K_D can be noncoincident, thus reflecting the influence of the temperature coefficients $V_{1,m}$ and $c_{g,\infty}$ on the temperature dependence of the solubility of simple gases in liquids.

The high accuracy of Eq. (5) is the result of internal consistency and, hence, reliability of the most part of the values[4—7] of nitrogen solubility in *n*-alkanes.

This fact makes it possible to use the system of Eqs (5) and (7) for the estimation of the reliability of other data on the nitrogen solubility in *n*-alkanes.

As an example let us consider the work[9] in which Henry´s constants of nitrogen in hexane at 303—393 K were calculated from the baric dependence of its molar fraction in the liquid phase in the region of partial gas pressures 0.22—34 bar. The statistical method was used for the saturation of the liquid with the gas, and the equilibrium composition of the liquid phase was calculated by a procedure described earlier.[10]

These dependences can be described by the equations

$$x_2 = (1.37\pm0.04)\cdot10^{-3}P_g \text{ (303.55 K)}, \qquad (8)$$

$$x_2 = (1.50\pm0.02)\cdot10^{-3}P_g \text{ (348.15 K)}, \qquad (9)$$

$$x_2 = (1.80\pm0.06)\cdot10^{-3}P_g \text{ (393.30 K)}. \qquad (10)$$

The values of nitrogen solubility at P_g = 1.01325 bar are compared in Table 2 with the values calculated by Eqs (5) and (7).

It is seen that at 303.55 K the both n_2 values nearly coincide, but at high temperatures the experimental values are higher. This suggests some systematic inaccuracy increasing with temperature in the procedure of calculation of x_2, which has been used earlier.[9]

In conclusion it should be noted that, when the solubility of nitrogen and noble gases in *n*-alkanes is expressed through Henry´s constants, the temperature dependences of the latter for different members of the homological series never coincide.[11—14]

A reason for similar situation becomes clear if Eq. (7) is compared with the equation

$$x_2 = (1/K_H)P_g = RTc_{g,\infty}/K_H, \qquad (11)$$

which is valid at $P_g \le 0.1$ MPa.

In this region of solubility of helium, neon, nitrogen, and even argon in *n*-alkanes, $x_2 \approx n_2$ and, hence, one can write

$$K_H = RT/(K_D V_{1,f}^*), \qquad (12)$$

$$\frac{dK_H}{dT} = R\left[\frac{K_D V_{1,f}^* - T\left(\frac{dK_D}{dT}V_{1,f}^* + \frac{dV_{1,f}^*}{dT}K_D\right)}{(K_D V_{1,f}^*)^2}\right], \qquad (13)$$

where $V_{1,f}^* = V_{1,m}(k^* - k)$.

It is seen that the temperature coefficient of Henry´s constant is a complex function of the temperature coefficients K_D and $V_{1,f}^*$, absolute values of these magnitudes, and temperature.

Table 2. Temperature dependence of the solubility of nitrogen in hexane under atmospheric pressure according to published data[9]

T/K	K_D	$c_{g,\infty}$ /mol m^{-3}	$V_{1,m}$	$V_{1,f}$	k	$n_2\cdot10^3$/mol mol^{-1}	
			10^{-6} m^3 mol^{-1}			Calculation	Experiment
303.55	2.44	40.148	132.61	13.87	0.5214	1.36	1.39±0.04
348.15	2.01	35.004	141.92	19.70	0.4872	1.39	1.52±0.02
393.30	1.75	30.986	154.80	27.77	0.4466	1.51	1.82±0.06

Due to this, Henry´s constant cannot be considered as the true characteristic of the affinity of gases to liquids, and the thermodynamic parameters obtained on the basis of the temperature dependence of the solubility should be treated as a result of two processes: the transfer of gas particles from the intrinsic phase to cavities of the intermolecular volume of the liquid and the change in the total volume of the latter due to the thermal expansion (compression) of the liquid.

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