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USE OF THE MODIFIED WILSON EQUATION FOR DESCRIPTION OF VAPOR–LIQUID EQUILIBRIUM IN THE SYSTEM 1-NONYNE–1-PROPANOL

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ABSTRACT

A modified Wilson equation is reported describing the linear dependence of the parameters $\lambda_{12}-\lambda_{11}$ and $\lambda_{21}-\lambda_{22}$ on temperature. The expressions for 16 partial derivatives of the minimization function have been derived in order to calculate the Wilson equation parameters from isobaric experimental data using the Newton iteration method. The modified Wilson method has been applied to T–x measurements for the 1-nonyne–1-propanol system. Experimental T–x data at pressures 100, 200, 400, 600 and 760 mm Hg are reported. Using the temperature-dependent Wilson parameters, the excess Gibbs energy is calculated at a temperature of 313.15 K and considered together with experimental excess enthalpy data.

INTRODUCTION

Wilson's equation [1] has been widely used to describe vapor–liquid equilibria and is still of importance today, though several more complicated models (e.g. NRTL, UNIQUAQ, etc.) have been developed.

In our opinion, it is possible to significantly increase the reliability of Wilson's equation, by considering accurately the temperature dependences of the Wilson parameters (Λ_{ij}, $\lambda_{ij}-\lambda_{ii}$) and ratios of molar volumes.

Normally, for binary systems, Wilson's equation serves as two parametric models. In order to estimate these parameters by regression two versions have been used. For not-too-large temperature intervals:

(a) the dependence of Λ_{ij} on temperature is ignored; two parameters, Λ_{12} and Λ_{21}, are found and related to the mean temperature of the interval used;

(b) Λ_{ij} is regarded as a function

$$\Lambda_{ij}=\frac{V_j}{V_i}\exp\left(-\frac{\lambda_{ij}-\lambda_{ii}}{RT}\right) \quad (1)$$

In the present case, the two estimated parameters are the Wilson constants $\lambda_{12}-\lambda_{11}$ and $\lambda_{21}-\lambda_{22}$.

In reality, the Wilson constants are not constant but depend on temperature. It has been shown that this dependence is linear [2], or nearly linear [3]. Evidently, the assumption that $\lambda_{ij} - \lambda_{ii}$ depends linearly on temperature may be regarded as quite a good approximation.

Wilson's equation provides a good representation of the excess Gibbs energy for a variety of completely miscible mixtures and is particularly useful for highly asymmetric systems, such as solutions of polar or associating components in non-polar or slightly polar solvents.

In previous publications by our laboratory, measurements of the vapor–liquid equilibria of isomeric alkynes with a number of hydrocarbons have been described [4–6].

The purpose of the present work is to apply the modified Wilson equation to the 1-nonyne–1-propanol vapor–liquid equilibrium at constant pressure. We are not aware of any previous determination of the vapor–liquid equilibrium of this system.

THEORY

The values of the parameters $\lambda_{12} - \lambda_{11}$, $\lambda_{21} - \lambda_{22}$, Λ_{12} and Λ_{21} are expressed as follows

$$\lambda_{12} - \lambda_{11} = m_1 + n_1 T \tag{2}$$

$$\lambda_{21} - \lambda_{22} = m_2 + n_2 T \tag{3}$$

$$\Lambda_{12} = \frac{V_2}{V_1} \exp[-(m_1 + n_1 T)/RT] \tag{4}$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp[-(m_2 + n_2 T)/RT] \tag{5}$$

We recommend describing the vapor–liquid equilibrium of binary systems by means of a modified Wilson equation containing four parameters: m_1, m_2, n_1 and n_2, which considers more exactly (compared with two-parameter models) the dependence of Λ_{12} and Λ_{21} on temperature. Of course, the ratio of liquid molar volumes should be regarded as a function of temperature function as well, though this dependence is unimportant.

To calculate the Wilson equation parameters from isobaric experimental data the following minimization function is often used (e.g. ref. 7)

$$\mathscr{D} = \sum_{i=1}^{n} \left(U_{\text{calcd}(i)} - U_{\text{exptl}(i)}\right)^2 = \min \tag{6}$$

where U_{calcd} and U_{exptl} are the calculated and experimental values of the mixture property.

The following equation system must be solved

$$\left.\begin{aligned} F_1 &= \frac{\partial \mathscr{D}}{\partial m_1} = 0 \\ F_2 &= \frac{\partial \mathscr{D}}{\partial n_1} = 0 \\ F_3 &= \frac{\partial \mathscr{D}}{\partial m_2} = 0 \\ F_4 &= \frac{\partial \mathscr{D}}{\partial n_2} = 0 \end{aligned}\right\} \tag{7}$$

The solutions of system (7) can be found using different iteration methods. We have chosen the Newton method for this purpose. In this case, the partial derivatives of the second degree of dispersion $\mathscr{D}$ (16 derivatives) must be expressed as well.

For a single set of experimental data (mole fractions in the liquid phase x_1 and x_2, temperature T at pressure P_{exptl}) the minimization function is

$$g = \left(P_{\text{calcd}} - P_{\text{exptl}}\right)^2 \tag{8}$$

where P_{calcd} is the sum of the partial pressures

$$P_{\text{calcd}} = P_1 + P_2 = P_1^{\circ} x_1 \gamma_1 \phi_1 + P_2^{\circ} x_2 \gamma_2 \phi_2 \tag{9}$$

and P_i°, γ_i and ϕ_i are the vapor pressure of the pure component i, its activity coefficient in the mixture and the correction factor for vapor-phase non-idealities, respectively.

In the present work the total pressure is calculated neglecting the vapor-phase non-ideality effect ($\phi_i = 1$), since the virial coefficients for 1-nonyne and its mixtures are not known. They can be determined only approximately and the estimation of critical properties of heavy hydrocarbons is uncertain [8].

We give the expressions of partial derivatives of the first and second degree for function (8); in the practical calculation these values must be found for each set of data and summarized. Using the approximate values of the coefficients m_1, n_1, m_2 and n_2 in each step of iteration, the values of Λ_{12} and Λ_{21} (see eqns. (4–5)) and all derivatives can be found.

For binary systems

$$\gamma_1 = \exp(q_1 + x_2 Z) \tag{10}$$

$$\gamma_2 = \exp(q_2 + x_1 Z) \tag{11}$$

where

$$Z = \Lambda_{12}/Z_1 - \Lambda_{21}/Z_2 \tag{12}$$

$$Z_1 = x_1 + x_2 \Lambda_{12} \tag{13}$$

$$Z_2 = x_2 + x_1\Lambda_{21} \tag{14}$$

$$q_1 = -\ln Z_1 \tag{15}$$

$$q_2 = -\ln Z_2 \tag{16}$$

The partial derivatives $\partial g/\partial\Lambda_{12}$ and $\partial g/\partial\Lambda_{21}$ may be defined by the following expressions

$$f_A = \frac{\partial g}{\partial\Lambda_{12}} = -2\ \Delta P x_1 x_2 Q_1/Z_1^2 \tag{17}$$

$$f_B = \frac{\partial g}{\partial\Lambda_{21}} = -2\ \Delta P x_1 x_2 Q_2/Z_2^2 \tag{18}$$

where

$$\Delta P = P_{\text{calcd}} - P_{\text{exptl}} \tag{19}$$

$$Q_1 = P_1^{\text{o}} x_2 \gamma_1 \Lambda_{12} + P_2^{\text{o}} x_1 \gamma_2 \tag{20}$$

and

$$Q_2 = P_1^{\text{o}} x_2 \gamma_1 + P_2^{\text{o}} x_1 \gamma_2 \Lambda_{21} \tag{21}$$

By means of $\partial g/\partial\Lambda_{12}$ and $\partial g/\partial\Lambda_{21}$ (f_A and f_B) values it is easy to express the following partial derivatives

$$f_1 = \frac{\partial g}{\partial m_1} = -\frac{\Lambda_{12}}{RT} f_A \tag{22}$$

$$f_2 = \frac{\partial g}{\partial n_1} = -\frac{\Lambda_{12}}{R} f_A \tag{23}$$

$$f_3 = \frac{\partial g}{\partial m_2} = -\frac{\Lambda_{21}}{RT} f_B \tag{24}$$

$$f_4 = \frac{\partial g}{\partial n_2} = -\frac{\Lambda_{21}}{R} f_B \tag{25}$$

To find the partial derivatives of f_1–f_4 in relation to m_1, n_1, m_2 and n_2 it is a rational first step to give the equations for $\partial f_A/\partial\Lambda_{12}$, $\partial f_A/\partial\Lambda_{21}$, $\partial f_B/\partial\Lambda_{12}$ and $\partial f_B/\partial\Lambda_{21}$

$$\frac{\partial f_A}{\partial\Lambda_{12}} = \frac{-2\ \Delta P x_1 x_2}{Z_1^2}\left[P_1^{\text{o}} x_2 \gamma_1 \left(1 - \frac{x_2^2\Lambda_{12}^2}{Z_1^2}\right) - P_2^{\text{o}} \frac{x_1^3}{Z_1^2}\gamma_2\right] + \frac{2Q_1 x_1 x_2^2}{Z_1^4}(x_1 Q_1 + 2Z_1\ \Delta P) \tag{26}$$

TABLE 1

Expressions for the partial derivatives $\partial f_i/\partial x$

i/x	m_1	n_1	m_2	n_2
1	$\frac{\Lambda_{12}}{(RT)^2} f_C$	$\frac{\Lambda_{12}}{R^2 T} f_C$	$\frac{\Lambda_{12}\Lambda_{21}}{(RT)^2} \frac{\partial f_A}{\partial \Lambda_{21}}$	$\frac{\Lambda_{12}\Lambda_{21}}{R^2 T} \frac{\partial f_A}{\partial \Lambda_{21}}$
2	$= \frac{\partial f_1}{\partial n_2}$	$\frac{\Lambda_{12}}{R^2} f_C$	$= \frac{\partial f_1}{\partial n_2}$	$\frac{\Lambda_{12}\Lambda_{21}}{R^2} \frac{\partial f_A}{\partial \Lambda_{21}}$
3	$= \frac{\partial f_1}{\partial m_2}$	$= \frac{\partial f_1}{\partial n_2}$	$\frac{\Lambda_{21}}{(RT)^2} f_D$	$\frac{\Lambda_{21}}{R^2 T} f_D$
4	$= \frac{\partial f_1}{\partial n_2}$	$= \frac{\partial f_2}{\partial n_2}$	$= \frac{\partial f_3}{\partial n_2}$	$\frac{\Lambda_{21}}{R^2} f_D$

$\partial f_A/\partial \Lambda_{21}$ and $\partial f_B/\partial \Lambda_{12}$ are equal

$$\frac{\partial f_A}{\partial \Lambda_{21}} = \frac{\partial f_B}{\partial \Lambda_{12}} = \frac{2x_1x_2}{Z_1^2 Z_2^2}\left[\Delta P\left(P_1^o x_2^3 \gamma_1 \Lambda_{12} + P_2^o x_1^3 \gamma_2 \Lambda_{21}\right) + x_1 x_2 Q_1 Q_2\right] \tag{27}$$

$$\frac{\partial f_B}{\partial \Lambda_{21}} = \frac{-2\ \Delta P x_1 x_2}{Z_2^2}\left[P_2^o x_1 \gamma_2 \left(1 - \frac{x_1^2 \Lambda_{21}^2}{Z_2^2}\right) - P_1^o \frac{x_2^3}{Z_2^2}\gamma_1\right] + \frac{2Q_2 x_2 x_1^2}{Z_2^4}\left(x_2 Q_2 + 2Z_2\ \Delta P\right) \tag{28}$$

Finally, 16 partial derivatives needed for the use of the Newton iteration method can be found. Taking

$$f_C = f_A + \Lambda_{12}\frac{\partial f_A}{\partial \Lambda_{12}} \tag{29}$$

$$f_D = f_B + \Lambda_{21}\frac{\partial f_B}{\partial \Lambda_{21}} \tag{30}$$

the results presented in Table 1 can be obtained.

Consequently, to find the values of parameters m_1, n_1, m_2 and n_2 from experimental data, for each set of data the values f_1–f_4 (eqns. (22–25)) and their partial derivatives (Table 1) have to be calculated and summarized, then the linear equation system with the symmetrical matrix must be solved in each step of iteration until the described precision is achieved.

EXPERIMENTAL

Materials and methods

1-Nonyne was synthesized in our laboratory, distilled at subatmospheric pressure in a high efficiency Teflon bristle-rotor column, and stored under argon protected from light. The purity of the 1-nonyne, tested by capillary gas chromatography, was not less than 99.5%. 1-Propanol (Reakhim, Kharkov, U.S.S.R., "puriss" grade) was used without further purification and stored in specially designed flasks isolated from external moisture.

Boiling temperatures are measured at constant pressures in a semimicrobulliometer. The details of the apparatus and experimental procedure have been described previously [9]. The error in the determination of boiling points is estimated to be less than 0.05 K. The binary mixtures were prepared by adding the weighted amounts of components. The mole fraction error is estimated to be less than 5×10^{-4}.

RESULTS AND DISCUSSION

The boiling temperatures determined at pressures of 100, 200, 400, 600 and 760 mm Hg are listed in Table 2 depending on mole fraction (x) of 1-nonyne along with the Wilson equation calculations. The experimental (exp) and calculated (calc) data are grouped in eleven columns, including liquid (x) and vapor (y) composition, boiling temperature, molar volume ratio, generalized Wilson parameters, total pressures and relative errors in calculated pressure.

We have found that when treating experimental data by use of the classical Wilson equation and the modified one given in this paper, the calculated sum of quadratic deviations $\Sigma(P_{\text{calcd}} - P_{\text{exptl}})^2$ by the latter is usually 2–10 times smaller (for the system 1-nonyne–1-propanol about 9 times).

The vapor pressures of the pure components were computed using the Antoine equation and the molar volume ratio from the linear equation; all the constants used are summarized in Table 2. The volumetric data used in this study were obtained from the pure component densities in the 298.15–333.15 K range [10].

Taking into account the temperature-dependent molar volume ratio and $\lambda_{ij} - \lambda_{ii}$ constants the generalized Wilson parameters in a temperature-dependent form may be given by

$$\Lambda_{12} = \frac{1}{2.1788 + 1.0985 \times 10^{-4} T} \exp\left(- \frac{-12.28 + 0.041T}{0.0083143T} \right) \tag{31}$$

$$\Lambda_{21} = 2.1788 + 1.0985 \times 10^{-4} T \exp\left(- \frac{17.64 - 0.0404T}{0.0083143T} \right) \tag{32}$$

These parameters can then be used in the Wilson model to predict the activity coefficients and hence vapor–liquid equilibrium data at a temperature of interest not far from the experimental temperature.

Wilson proposed the following expression for the excess Gibbs energy in the binary system

$$\frac{G^{\mathrm{E}}}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2(x_2 + \Lambda_{21}x_1) \tag{33}$$

For the system 1-nonyne–1-propanol the experimental data of T–x and that of the mixing enthalpy determined previously [11] were quite far from each other in temperature. In order to consider simultaneously the excess thermodynamic functions, G^{E} was estimated by means of eqns. (31)–(33) at 313.15 K, at which temperature the H^{E} data were measured [11]. Using the well-known equation

$$TS^{\mathrm{E}} = H^{\mathrm{E}} - G^{\mathrm{E}} \tag{34}$$

the excess entropies were determined from the smoothed values of H^{E} and G^{E}. The results of calculations are shown in Fig. 1. The values of G^{E} are positive in all the 1-nonyne–1-propanol mixtures investigated. The behavior of H^{E} is more asymmetric than that of G^{E}, both functions behaving irregularly. $TS^{\mathrm{E}} - x$ is sigmoid and positive for $x > 0.35$.

It is interesting to note finally that the mixtures of alcohols with n-alkenes and alkylcyclenes studied previously [12] have an opposite arrangement of the $G^{\mathrm{E}} - x$ and $H^{\mathrm{E}} - x$ curves.

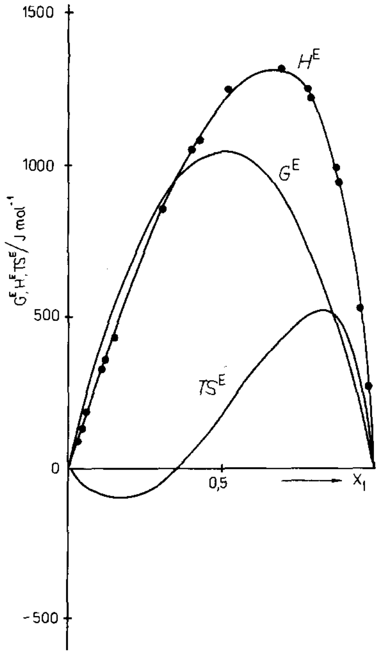

Fig. 1. Excess thermodynamic properties at 313.15 K for system 1-nonyne–1-propanol.

TABLE 2

Vapor–liquid equilibria in system 1-nonyne–1-propanol

Mole fractions		Boiling temp. (exp) (K)	Ratio of mol. vol. (calc) V_1/V_2	Generalized parameters (calc)		Activity coefficients (calc)		G^E (calc) (kJ mol^{-1})	Pressure (calc) (mm Hg)	Rel. error in pressure (%)
x_1 (exp)	y_1 (calc)			Λ_{12}	Λ_{21}	γ_1	γ_2			
0.000	0.000	324.980	2.2145	0.3072	0.4191	5.819	1.000	0.000	99.97	−0.03
0.127	0.079	325.240	2.2145	0.3061	0.4213	3.359	1.036	0.500	99.59	−0.41
0.297	0.120	325.670	2.2146	0.3043	0.4250	2.075	1.177	0.897	97.46	−2.54
0.489	0.147	326.830	2.2147	0.2994	0.4349	1.454	1.476	1.038	97.45	−2.55
0.687	0.185	329.900	2.2150	0.2870	0.4621	1.149	2.036	0.872	100.93	0.93
0.867	0.300	337.490	2.2159	0.2594	0.5342	1.023	2.842	0.445	101.54	1.54
1.000	1.000	362.010	2.2186	0.1927	0.8188	1.000	2.738	0.000	100.04	0.04
0.000	0.000	338.790	2.2160	0.2551	0.5473	6.164	1.000	0.000	200.14	0.07
0.127	0.077	339.210	2.2161	0.2537	0.5515	3.251	1.041	0.522	200.98	0.49
0.297	0.112	339.630	2.2161	0.2524	0.5558	1.953	1.190	0.906	196.22	−1.89
0.489	0.140	341.200	2.2163	0.2473	0.5721	1.379	1.480	1.014	197.14	−1.43
0.687	0.186	345.290	2.2167	0.2349	0.6159	1.115	1.952	0.815	203.13	1.56
0.867	0.331	355.660	2.2179	0.2073	0.7372	1.015	2.424	0.387	205.19	2.60
1.000	1.000	380.530	2.2206	0.1578	1.0900	1.000	2.130	0.000	199.83	−0.08
0.000	0.000	354.190	2.2177	0.2109	0.7191	6.279	1.000	0.000	399.95	−0.01
0.127	0.071	354.860	2.2178	0.2092	0.7273	3.017	1.046	0.530	404.41	1.10
0.297	0.103	355.530	2.2179	0.2076	0.7356	1.791	1.197	0.885	396.96	−0.76

0.489	0.133	357.580	2.2181	0.2027	0.7612	1.294	1.460	0.949	396.85	−0.79
0.687	0.192	362.920	2.2187	0.1907	0.8309	1.081	1.811	0.722	401.74	0.43
0.867	0.374	376.570	2.2202	0.1644	1.0277	1.009	1.986	0.310	406.26	1.57
1.000	1.000	401.770	2.2229	0.1284	1.4652	1.000	1.632	0.000	400.46	0.12
0.000	0.000	364.080	2.2188	0.1882	0.8466	6.193	1.000	0.000	599.86	−0.02
0.127	0.066	364.930	2.2189	0.1865	0.8582	2.822	1.049	0.525	608.08	1.35
0.297	0.097	365.850	2.2190	0.1846	0.8709	1.680	1.197	0.853	599.12	−0.15
0.489	0.130	368.390	2.2193	0.1795	0.9065	1.241	1.434	0.887	597.68	−0.39
0.687	0.198	374.610	2.2200	0.1679	0.9978	1.062	1.703	0.647	595.75	−0.71
0.867	0.404	390.610	2.2217	0.1427	1.2593	1.006	1.731	0.253	606.32	1.05
1.000	1.000	415.550	2.2244	0.1136	1.7468	1.000	1.389	0.000	599.67	−0.06
0.000	0.000	370.190	2.2195	0.1760	0.9323	6.080	1.000	0.000	760.09	0.01
0.127	0.063	371.160	2.2196	0.1742	0.9465	2.690	1.050	0.519	771.24	1.48
0.297	0.093	372.290	2.2197	0.1721	0.9631	1.612	1.195	0.826	762.05	0.27
0.489	0.129	375.200	2.2200	0.1668	1.0067	1.210	1.412	0.841	759.06	−0.12
0.687	0.203	382.020	2.2208	0.1554	1.1141	1.051	1.631	0.595	749.25	−1.41
0.867	0.424	399.240	2.2227	0.1315	1.4168	1.004	1.592	0.217	761.02	0.13
1.000	1.000	424.210	2.2254	0.1056	1.9395	1.000	1.261	0.000	760.15	0.02

Values of the principal parameters: $\lambda L_{12} - \lambda L_{11} = -12.277 + 0.04098T$ kJ mol^{-1}; $\lambda L_{21} - \lambda L_{22} = 17.64 - 0.04044T$ kJ mol^{-1}.

Root-mean error in pressure, 4.03.

Coefficients of Antoine equation ($\ln P = A + B/(C+T)$): 1-nonyne—$A = 15.79138$, $B = -3141.9340$, $C = -81.124$; 1-propanol—$A = 17.72940$, $B = -3245.5370$, $C = -77.693$.

Coefficients of the ratio of molar volumes ($V_1/V_2 = R_1 + R_2T$): $R_1 = 2.1788$, $R_2 = 1.0985 \times 10^{-4}$.

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