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THE WILSON PARAMETERS FOR *n*-HEXANE MIXTURES OF THE LOWEST PRIMARY AND SECONDARY ALIPHATIC AMINES STUDIED BY THE CONTOUR LINES OF THEIR ERROR SQUARES

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ABSTRACT

For *n*-hexane mixtures of the lowest primary and secondary aliphatic amines the interdependence of the Wilson parameters $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ and of the objective function Q minimized in the parameter evaluation by regression was studied in three- and two-dimensional representations. The diagrams containing the contour lines of $-Q$ as a function of $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ show a reasonably well-defined maximum for the mixtures with methyl-, ethyl- and *n*-propylamine, but almost a plateau for those with dimethyl-, methylethyl- and diethylamine. For the latter compounds this leads to a multiplicity of Wilson pairs which describe the vapour pressure function, to an uncertainty of the parameters with respect to their interpretation as quantities which reflect the pair interactions, and to the possibility of a one-parametric representation of the activity coefficients without modifying the Wilson equations. The differences between the systems with the lowest secondary amines and those with the primary analogues are related to the weaker self-association or the smaller deviations from Raoult's law of the former.

INTRODUCTION

For *n*-hexane mixtures of the lowest primary and secondary aliphatic amines, the data from isothermal vapour pressure measurements could be reduced according to the relation

$$P = \sum_{i=1}^{2} \frac{x_i \gamma_i P_i^0 \phi_i^0 \Omega_i}{\phi_i} \tag{1}$$

where x_i denotes the mole fractions of the binary mixture, γ_i the activity coefficients, Ω_i the Poynting corrections, P_i^0 and ϕ_i^0 the vapour pressures and the fugacity coefficients of the pure components at saturation respec-

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tively, and ϕ_i the fugacity coefficients in the gaseous mixture [1–7]. Wilson's equations [8–10]

$$\gamma_1 = (x_1 + \Lambda_{12}x_2)^{-1} \exp\left[x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)\right] \tag{2a}$$

and

$$\gamma_2 = (x_2 + \Lambda_{21}x_1)^{-1} \exp\left[-x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)\right] \tag{2b}$$

with

$$\Lambda_{12} = \left(V_2^{0L}/V_1^{0L}\right) \exp[(\lambda_{12} - \lambda_{11})/RT] \tag{3a}$$

and

$$\Lambda_{21} = \left(V_1^{0L}/V_2^{0L}\right) \exp[(\lambda_{12} - \lambda_{22})/RT] \tag{3c}$$

where V_1^{0L} and V_2^{0L} denote the molar volumes of the pure liquid components, proved to be appropriate in representing the activity coefficients [3,5–7]. Simultaneously, the Wilson parameters $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ could be interpreted from the idea [11] that the λs are negative quantities reflecting the pair interactions indicated by the suffixes. If 1 refers to the amine and 2 to the hydrocarbon, then according to this explanation the fact that $(\lambda_{12} - \lambda_{11})$ is positive confirms that the interaction through hydrogen bonds between the amine molecules is greater than that through unspecific intermolecular forces between the amine and the hydrocarbon molecules. Moreover, the fact that $(\lambda_{12} - \lambda_{11})$ is 1000–2300 J mol^{-1} for the mixtures of dimethyl-, methylethyl- and diethylamine and is significantly smaller than the value for methyl-, ethyl- and *n*-propylamine of 2400–4000 J mol^{-1} (at 293 K) indicates the weaker hydrogen bonds of the former.

INVESTIGATIONS

To increase knowledge of the quality and interpretation of the reported Wilson parameters, the interdependence of the parameters and the objective function minimized in their evaluation by regression [12] should now be examined. The objective function was *

$$Q = \sum_{i=1}^{n} (\overline{P} - P)^2 \tag{4}$$

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* Applying eqn. (1) to amine–hexane mixtures,

$$\Omega_i = \exp\left[V_i^{0L}(P - P_i^0)/RT\right] \tag{5}$$

can be inserted while ϕ_i^0 and ϕ_i can be taken from a virial approach for the gas phase considering only second virial coefficients.

where $\overline{P}$ denotes the measured pressures of the mixtures and n the number of data points. In fact, a consideration of $-Q$ is more appropriate because in the diagrams used for the analysis a maximum is observed more clearly than a minimum. Therefore, computer programs were utilized to calculate Q as a function of $(\lambda_{12}-\lambda_{11})$ and $(\lambda_{12}-\lambda_{22})$ and to plot lines with equal values of $-Q$ over these coordinates in three- and two-dimensional representations. In the three-dimensional diagrams, showing the hypersurface of $-Q$ in a perspective way, 40 equidistant contour lines were reproduced. This was achieved with data of $-Q$ at the 500 × 500 points, which could be calculated if ranges of the two parameters in the region of the maximum of approximately 1300 J mol^{-1} were divided into 500 equal intervals. For the two-dimensional diagrams, also showing 40 equidistant contour-lines, the ranges of approximately 1300 J mol^{-1} were divided in 100 equal intervals.

RESULTS

Figure 1 gives the diagrams of the hexane mixtures of trideuteromethanol at 323 K, trideuteromethylamine at 293 K, propylamine at 253 K and

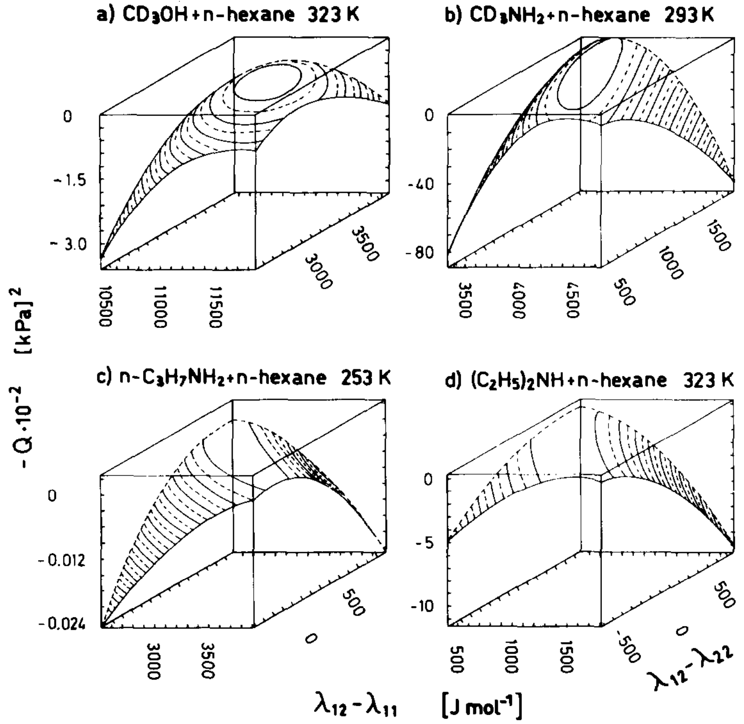

Fig. 1. Three-dimensional representation of the objective function Q as a function of $(\lambda_{12}-\lambda_{11})$ and $(\lambda_{12}-\lambda_{22})$ for (a) CD_3OH + n-hexane at 323 K, (b) CD_3NH_2 + n-hexane at 293 K, (c) n-$C_3H_7NH_2$ + n-hexane at 253 K, (d) $(C_2H_5)_2NH$ + n-hexane at 323 K.

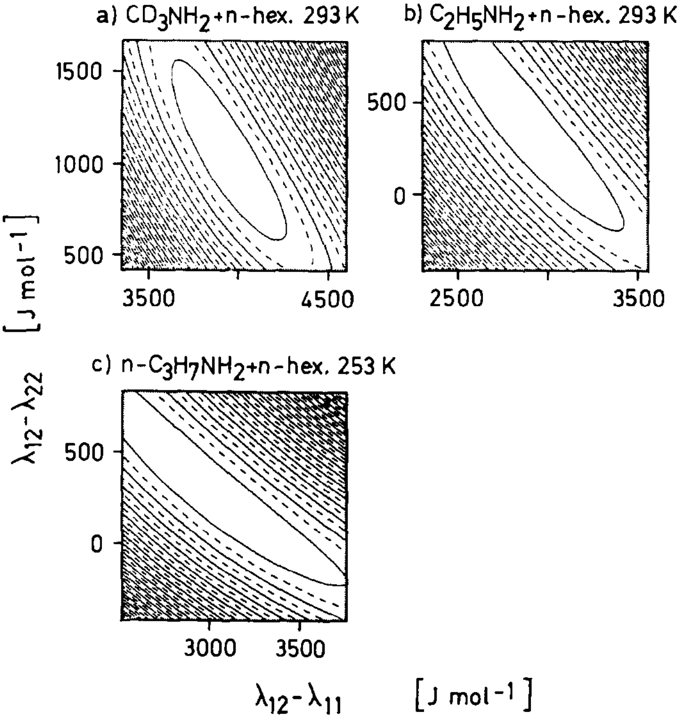

Fig. 2. Two-dimensional representation of the objective function over the coordinates $(\lambda_{12}-\lambda_{11})$ and $(\lambda_{12}-\lambda_{22})$ for (a) CD_3NH_2 + *n*-hexane at 293 K, (b) $C_2H_5NH_2$ + *n*-hexane at 293 K, (c) *n*-$C_3H_7NH_2$ + *n*-hexane at 253 K.

diethylamine at 323 K [1,2,5,6]. The strongly associated methanol mixtures are considered for comparison; the contour lines show that for this system (Fig. 1(a)) the hypersurface of $-Q$ has a vault-like form and therefore a defined maximum. This is observed to be somewhat less pronounced for the methylamine system (Fig. 1(b)). The hypersurface of the propylamine mixtures (Fig. 1(c)) corresponds to the transition to the diethylamine mixtures (Fig. 1(d)) showing almost a plateau instead of a well-defined maximum.

In the two-dimensional representation Figs. 2 and 3 compare the diagrams of trideuteromethylamine–, ethylamine– and propylamine–hexane at 293 or 253 K [1,2] with those of hexadeuterodimethylamine–, methylethylamine– and diethylamine–hexane at 293 or 323 K [4,5]. In accordance with the three-dimensional representations, the systems with the primary amines show a reasonably well-defined maximum of $-Q$ but those for the secondary amines show instead of a maximum almost a plateau whose main direction forms an angle of about $-45°$ with the axes of the $(\lambda_{12}-\lambda_{11})$ vs. $(\lambda_{12}-\lambda_{22})$ diagram. The propylamine mixtures again behave intermediately.

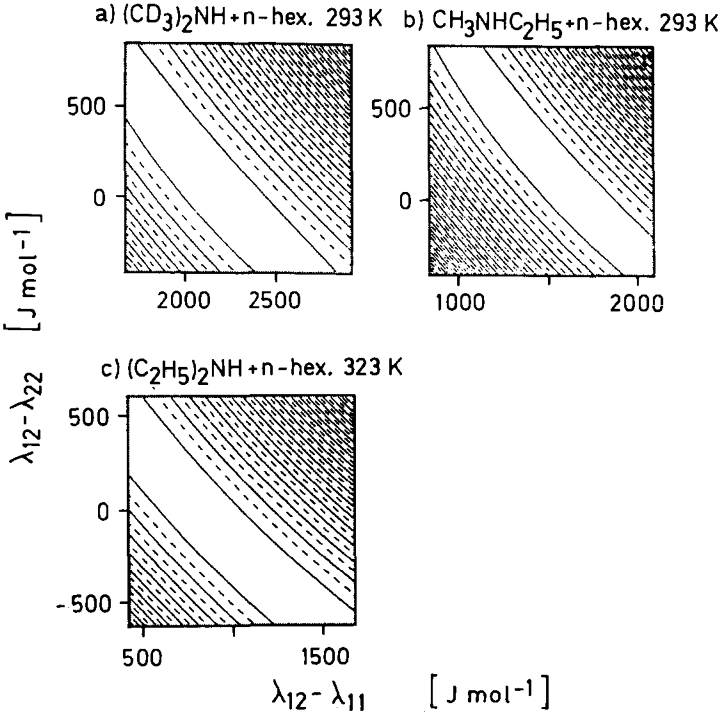

Fig. 3. Two-dimensional representation of the objective function over the coordinates $(\lambda_{12}-\lambda_{11})$ and $(\lambda_{12}-\lambda_{22})$ for (a) $(CD_3)_2NH$ + *n*-hexane at 293 K, (b) $(CH_3)NH(C_2H_5)$ + *n*-hexane at 293 K, (c) $(C_2H_5)_2NH$ + *n*-hexane at 323 K.

DISCUSSION

The determination of a defined maximum for the mixtures with the primary amines proves that at a given error limit the Wilson parameters can vary within a small range of values only. The determination of almost a plateau for the mixtures with the secondary amines, however, means that a large range of Wilson parameters describe the vapour pressure function. This observation agrees with the results of investigations [13–16] in which other objective functions, e.g. involving the experimental and calculated activity coefficients or the excess Gibbs energies, were minimized instead of Q defined by eq. 4. They led to Wilson parameters whose values differed significantly, but reproduced the experimental data for the most part equally well.

The existence of strongly differing pairs of Wilson parameters for the same isotherm suggests that the explanation of the λs as quantities which reflect the interactions between the two components of the mixtures is limited. The limitation does not affect the conclusion for the weaker association of the secondary amines, but it has to be considered when comparing the parameters listed in Table 1 for $(CH_3)NH(C_2H_5)$–hexane and

TABLE 1

Wilson parameters $(\lambda_{12}-\lambda_{11})$ and $(\lambda_{12}-\lambda_{22})$ [a] and their sum $S=(2\lambda_{12}-\lambda_{11}-\lambda_{22})$ for binary mixtures of $(CH_3)NH(C_2H_5)$, $(CH_3)ND(C_2H_5)$, $(C_2H_5)_2NH$ and $(C_2H_5)_2ND$ (1) with *n*-hexane

T (K)	$\lambda_{12}-\lambda_{11}$ (J mol^{-1})	$\lambda_{12}-\lambda_{22}$ (J mol^{-1})	S (J mol^{-1})	$\lambda_{12}-\lambda_{11}$ (J mol^{-1})	$\lambda_{12}-\lambda_{22}$ (J mol^{-1})	S (J mol^{-1})
	$(CH_3)NH(C_2H_5)$ + *n*-hexane			$(CH_3)ND(C_2H_5)$ + *n*-hexane		
273.15	1617±83	525±97	2142	1909±64	218±64	2127
283.15	1677±41	196±44	1873	1829±44	73±44	1902
293.15	1595±34	100±37	1695	1734±37	7±37	1741
303.15	1516±33	47±36	1563	1628±35	−19±37	1609
313.15	1441±29	1±32	1442	1542±36	−60±39	1482
323.15	1406±35	−87±39	1319	1479±36	−116±39	1363
	$(C_2H_5)_2NH$ + *n*-hexane			$(C_2H_5)_2ND$ + *n*-hexane		
293.15	1005±224	103±229	1108	1379±239	−293±207	1086
303.15	1150±161	−141±153	1009	1252±154	−248±140	1004
313.15	1021±140	−97±139	924	1166± 95	−249± 89	917
323.15	994±119	−153±119	841	1090± 78	−241± 75	849
333.15	965±101	−192±101	773	972± 60	−190± 60	782
343.15	916± 81	−208± 82	708	912± 60	−192± 61	720
353.15	828±103	−140±108	688	751± 76	−38± 82	713

[a] From ref. 5.

$(CH_3)ND(C_2H_5)$–hexane and also for $(C_2H_5)_2NH$–hexane and $(C_2H_5)_2$ND–hexane. The parameter referring predominantly to the amine interaction, according to the present notation $(\lambda_{12}-\lambda_{11})$, is usually slightly greater for the system with the N-deuterated amine owing to a somewhat enhanced strength of the deuterium bond [6,7]. The enhanced deuterium bond strength appears to be indicated in Table 1 since for most isotherms $(\lambda_{12}-\lambda_{11})$ is considerably greater for the deuterated system. As shown subsequently, however, for the same isotherm an equivalent pair of Wilson parameters is also given by assuming $(\lambda_{12}-\lambda_{22})$ is zero and using the sum of the parameters obtained by regression for $(\lambda_{12}-\lambda_{11})$. These sums, also taken from Table 1, differ for the system with the NH- and the analogous ND-compound mainly within error limits, so that the uncertainty in the interpretation is evident.

For the methylethylamine and the diethylaminesystems, and similarly the dimethylaminesystem, assuming $(\lambda_{12}-\lambda_{22})$ is zero and using the sum of the parameters obtained by regression for $(\lambda_{12}-\lambda_{11})$ yields an equivalent pair of Wilson parameters since the activity coefficients calculated under these assumptions agree with the regularly calculated values (Table 2). Considering that when using the sum for the calculation the second parameter is zero, this agreement simultaneously proves the possibility of a one-parametric representation of the activity coefficients without introducing the vaporiza-

TABLE 2

Activity coefficients γ_1 and γ_2 for binary mixtures of $(CH_3)NH(C_2H_5)$ and $(C_2H_5)_2NH$ (1) with *n*-hexane (2) obtained from the Wilson equations (a) by using the values of $(\lambda_{12}-\lambda_{11})$ and $(\lambda_{12}-\lambda_{22})$ found by regression, (b) by setting $(\lambda_{12}-\lambda_{22})=0$ and using the sum of the parameters for $(\lambda_{12}-\lambda_{11})$ [a]

T (K)	x_1	From the parameters found by regression		From $(\lambda_{12}-\lambda_{22})=0$ and the sum of the parameters found by regression for $(\lambda_{12}-\lambda_{11})$		From the parameters found by regression		From $(\lambda_{12}-\lambda_{22})=0$ and the sum of the parameters found by regression for $(\lambda_{12}-\lambda_{11})$	
		γ_1	γ_2	γ_1	γ_2	γ_1	γ_2	γ_1	γ_2
		$(CH_3)NH(C_2H_5)$ + *n*-hexane				$(C_2H_5)_2NH$ + *n*-hexane			
293.15	0	1.85_3	1	1.85_8	1	1.52_3	1	1.53_7	1.00
	0.1	1.65_3	1.00_6	1.65_7	1.00_6	1.40_9	1.00_4	1.41_6	1.00_4
	0.2	1.49_3	1.02_4	1.49_5	1.02_4	1.31_3	1.01_7	1.31_6	1.01_7
	0.5	1.17_7	1.16_5	1.17_7	1.16_6	1.11_5	1.11_0	1.11_3	1.11_3
	1	1	1.93_1	1	1.93_5	1	1.55_1	1	1.53_9
323.15	0	1.53_5	1	1.51_9	1	1.34_9	1	1.33_6	1
	0.1	1.42_5	1.00_4	1.41_5	1.00_4	1.27_5	1.00_3	1.26_8	1.00_3
	0.2	1.33_1	1.01_6	1.32_6	1.01_5	1.21_2	1.01_2	1.20_9	1.01_9
	0.5	1.12_8	1.11_2	1.12_8	1.10_9	1.07_9	1.07_8	1.08_0	1.07_5
	1	1	1.62_4	1	1.62_8	1	1.35_4	1	1.36_3

[a] Values of the parameters found by regression and of their sum from Table 1.

tion energy [17] or the configurational energy [18] in the Wilson equations for the like pair interactions. Such a representation is impossible for the mixtures investigated with primary amines owing to the lack of a Wilson pair with $(\lambda_{12} - \lambda_{22})$ equal to zero near the line centre (Figs. 2(a)–2(c)).

Following former explanations [13], even a more sophisticated parameter evaluation such as the maximum likelihood method [19] cannot be expected to yield significantly different results. Therefore, with regard to the determination of a defined maximum at a stronger self-association the observation of almost a plateau for the mixtures with dimethyl-, methylethyl- and diethylamine can be linked to the low magnitude [4,5,20] of the positive deviations of these systems from Raoult's law. This also applies to the specific properties for the Wilson parameters resulting from the plateau-like character of the maxima. Accordingly, not only the lower values of $(\lambda_{12} - \lambda_{11})$, but also the multiplicity of the Wilson pairs, the uncertainty of their interpretation and the possibility of a one-parametric representation of the activity coefficients without modifying the Wilson equations, characterize the weaker hydrogen bonds of the lowest secondary amines in relation to their primary analogues.

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LIST OF SYMBOLS

n	number of data points
P	calculated total vapour pressure of mixture
$\bar{P}$	measured total vapour pressure of mixture
P_1^0, P_2^0	vapour pressures of pure components
Q	objective function (eq. 4)
R	universal gas constant
S	sum of Wilson parameters
T	temperature (K)
x_1, x_2	mole fractions in liquid phase
V_1^{0L}, V_2^{0L}	molar volumes of pure liquid components

Greek letters

γ_1, γ_2	activity coefficients
$(\lambda_{12} - \lambda_{11})$, $(\lambda_{11} - \lambda_{22})$	Wilson parameters

Λ_{12}, Λ_{21}	extended Wilson parameters (eqns. (3a) and (3b))
ϕ_1^0, ϕ_2^0	fugacity coefficients of pure components at saturation
ϕ_1, ϕ_2	fugacity coefficients of components in the gaseous mixture
Ω_1, Ω_2	Poynting corrections (eq. 5)

Indices

1	refers to amine in the liquid mixture
2	refers to hydrocarbon in the liquid mixture

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