Thermochimica Acta, 116 (1987) 267–274
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DESCRIPTION OF BINARY SYSTEMS CONTAINING HYDROCARBONS AND ALCOHOLS BY A MODIFIED NRTL EQUATION

PAWEŁ GIERYCZ

Instytut Chemii Fizycznej P.A.N., Kasprzaka 44/52, Warszawa (Poland)

(Received 11 December 1986)

ABSTRACT

The total pressure data for binary mixtures containing hydrocarbons (n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-undecane) and n-alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol) have been correlated by means of the NRTL equation and its modified [1] version making provisions for association.

The correlation results much improve with the use of the modified equation, achieving the accuracy of representation of the excess Gibbs energy for all systems under investigation within the error limits of original experiment.

INTRODUCTION

Although the problem of correlation and prediction of binary mixtures containing hydrocarbons and alcohols has been investigated for many years it is still not solved satisfactorily. There is no available model, based on theoretical assumptions (association models, local composition concept) or with an empirical background only, able to describe vapour–liquid equilibrium (VLE), within the accuracy which can be achieved experimentally, as a function of temperature and concentration for such systems.

The purpose of this work was to propose a thermodynamic model suitable to represent, with the desired accuracy, the thermodynamic properties of binary mixtures containing alcohols and hydrocarbons and to indicate a procedure for dealing with VLE data which are difficult to correlate.

CORRELATION

Calculations have been carried out for the following isothermal binary VLE data: (1) methanol–n-hexane at 313.15 K [2]; (2) methanol–n-octane at 313.15 K [3]; (3) ethanol–n-hexane at 313.15 K [2]; (4) ethanol–n-heptane at 313.15 K [4]; (5) ethanol–n-octane at 313.15 K [3]; (6) ethanol–n-nonane at 343.15 K [5]; (7) ethanol–n-undecane at 313.15 K [6]; (8) 1-propanol–n-

0040-6031/87/$03.50

heptane at 313.15 K [7]; (9) 1-propanol–n-octane at 313.15 K [3]; (10) 1-propanol–n-undecane at 333.15 K [7]; (11) 1-butanol–n-hexane at 313.15 K [3]; (12) 1-butanol–n-heptane at 323.15 K [8]; (13) 1-butanol–n-octane at 313.15 K [3]; (14) 1-pentanol–n-hexane at 313.15 K [3]; (15) 1-pentanol–n-heptane at 313.15 K [3]; (16) 1-pentanol–n-octane at 313.15 K [3]; (17) 1-pentanol–n-decane at 363.15 K [9].

Data for correlation have been chosen for a wide representation of various systems containing hydrocarbons and alcohols in a common temperature range. This means that we deal with systems formed both by "short" (methanol, ethanol) and "long" (1-pentanol) alcohols and by "short" (hexane) and "long" (undecane) hydrocarbons. Another criterion has been the accuracy and reliability of data. First the thermodynamic consistency of the data has been checked by three independent consistency tests proposed by Oracz [10]. Second we have tried to select data from only a few and the most reliable laboratories possible.

Such selected VLE data have been correlated by means of the NRTL equation. The calculations have been carried out for $\alpha = 0.3$ (arbitrarily chosen) and $\alpha = 0.45$ (mean value of α computed for all calculated systems). The computed values of root mean square deviations of pressure (eqn. 1) D(P) are given in Table 1 and Figs. 1 and 2.

$$D(\mathrm{P}) = \left[\frac{\sum_{i=1}^{n} (P_i \exp - P_i \mathrm{cal})^2}{n - m} \right]^{1/2} \tag{1}$$

where $P_i$exp, $P_i$cal are the experimental and calculated total vapour pressures, respectively, n is the number of experimental data points, and m is the number of adjustable parameters.

The analysis of the D(P) values shows that the poorest correlation results were obtained for systems where we deal with strong association i.e. at low temperatures and for "short" alcohols with "short" hydrocarbons (methanol–hexane, ethanol–heptane). The results confirm our previous statement that the NRTL equation fails to describe VLE in the systems with strong association well [1]. It could be expected that for these systems the modified [1] NRTL equation (NRTLMK) should give a better description. The NRTLMK equation which was derived by grouping the NRTL equation and the Mecke–Kempter equation [11] has the following form for the activity coefficient of the associating component (in this case alcohol)

$$\ln \gamma_1 = x_2^2 \left[\left(\frac{\tau_{21}\Gamma_{21}^2}{(x_1 + x_2\Gamma_{21})^2} \right) + \left(\frac{\tau_{12}\Gamma_{12}^2}{(x_2 + x_1\Gamma_{12})^2} \right) \right] + \left(\frac{1+K}{K} \right) \ln \left[\frac{1+K}{1+Kz_\mathrm{A}} \right] - z_\mathrm{B} \tag{2}$$

TABLE 1

Root mean square deviations of pressure $D(\mathrm{P})$ for all systems investigated

Equation	$D(\mathrm{P})$									
	Methanol		Ethanol		Propanol		Butanol		Pentanol	
	NRTL	NRTLMK	NRTL	NRTLMK	NRTL	NRTLMK	NRTL	NRTLMK	NRTL	NRTLMK
$\alpha = 0.3$										
n-Hexane	4.29	0.58	1.32	0.24			0.59	0.09	0.71	0.20
n-Heptane			0.87	0.12	0.47	0.06	0.23	0.13	0.21	0.09
n-Octane	1.72	0.85	0.62	0.05	0.14	0.01	0.08	0.08	0.07	0.01
n-Nonane			1.80	0.23						
n-Decane									0.06	0.05
n-Undecane			0.63	0.63	0.69	0.11				
$\alpha = 0.45$										
n-Hexane	1.73	0.34	0.63	0.22			0.36	0.08	0.49	0.19
n-Heptane			0.63	0.23	0.30	0.06	0.23	0.13	0.15	0.08
n-Octane	1.30	0.80	0.14	0.04	0.06	0.01	0.08	0.07	0.04	0.01
n-Nonane			0.59	0.19						
n-Decane									0.05	0.05
n-Undecane			0.89	0.66	0.39	0.10				

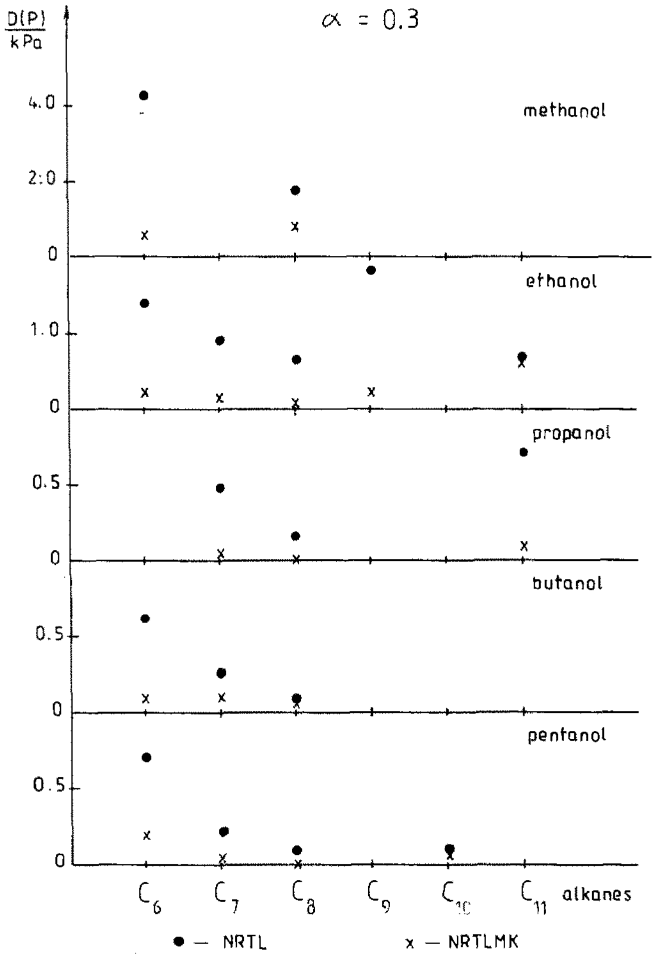

Fig. 1. Root mean square deviations of pressure D(P) for all systems investigated ($\alpha = 0.30$).

and for the activity coefficient of the non-associating component (in this case the hydrocarbon)

$$\ln \gamma_2 = x_1^2\left[\left(\frac{\tau_{12}\Gamma_{12}^2}{(x_2+x_1\Gamma_{12})^2}\right)+\left(\frac{\tau_{21}\Gamma_{21}^2}{(x_1+x_2\Gamma_{21})^2}\right)\right] - \left(\frac{r_{21}}{K}\right)\ln(1+Kz_A)+r_{21}z_A \qquad (3)$$

where $r_{ij} = V_i/V_j$, $z_A = r_{21}/(x_1+r_{21}x_2)$, $z_B = r_{21}x_2/(x_1+r_{21}x_2)$.

The NRTLMK equation which has only one adjustable parameter (K) more than the NRTL equation has been used for correlation of all investigated data. The values obtained for D(P) are given in Table 1 and Figs. 1 and 2. Table 2 shows the calculated values of parameter K.

TABLE 2

Calculated values of parameter K for all systems investigated

α	K									
	Methanol		Ethanol		Propanol		Butanol		Pentanol	
	0.30	0.45	0.30	0.45	0.30	0.45	0.30	0.45	0.30	0.45
n-Hexane	99.0	90.0	46.0	42.0			70.0	66.0	30.0	28.0
n-Heptane			93.0	89.0	78.0	77.0	36.0	36.0	50.0	46.0
n-Octane	67.0	65.0	87.0	79.0	45.0	43.0	14.0	13.0	44.0	43.0
n-Nonane			68.0	64.0						
n-Decane									4.0	4.0
n-Undecane			1.0	1.6	49.0	46.0				

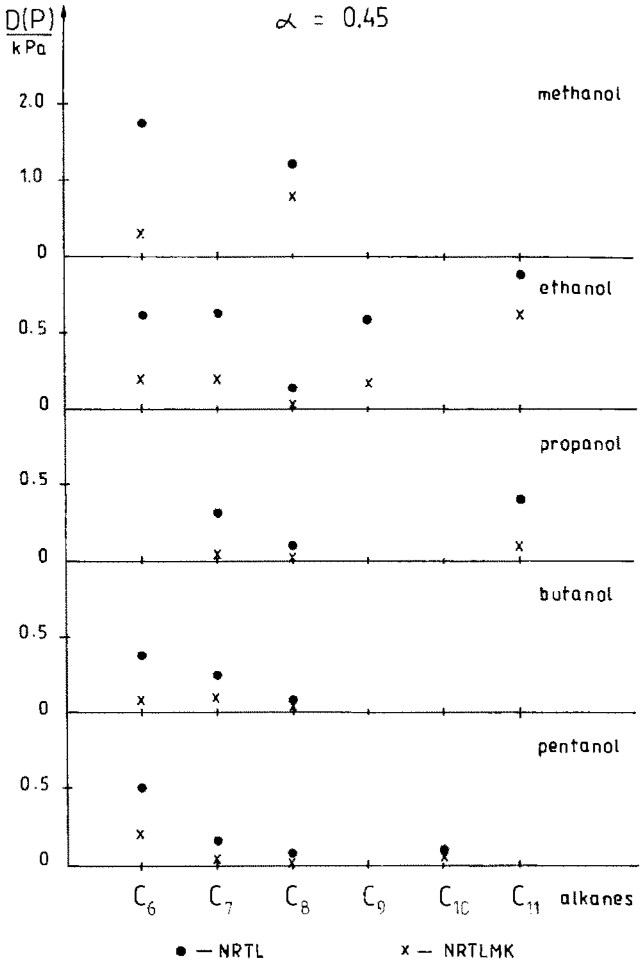

Fig. 2. Root mean square deviations of pressure $D(\mathrm{P})$ for all systems investigated ($\alpha = 0.45$).

The results of the correlation (Table 1) obtained by means of the NRTLMK equation are significantly better (sometimes almost 10 to 12-fold) than those using the NRTL equation. This means that an appropriate model was used for calculation of VLE for binary systems containing hydrocarbons and alcohols.

It is difficult to give a physical meaning to the values of K obtained (Table 2) but the good results of correlation justified the modification of the NRTL equation.

CONCLUSIONS

The good results of correlation which are similar to experimental accuracy for all systems investigated were obtained by the NRTLMK equation. This equation has one adjustable parameter (*K*) more than the NRTL equation for strongly-associating systems while for all other systems it reduces to a three parameter NRTL equation.

For systems where we deal with strong association (methanol, ethanol at 315.15 K—Table 1, Figs. 1 and 2) the second part of the NRTLMK equation (taken from the M–K model is significant) a high value of the *K* constant is obtained, which indicates that this part has considerable influence on correlation. On the other hand, for systems where association is weaker ("longer" hydrocarbons and alcohols (Table 1, Figs. 1 and 2)) the second part of the equation becomes unimportant (low values of the *K* constant) and the NRTLMK equation gives similar results to the NRTL equation.

The results of correlation of VLE for the systems investigated using the NRTLMK equation agree with results previously obtained for binary, strongly-associating systems [1] and justify the introduction of such a modification of the NRTL equation for calculation of the excess Gibbs energy in binary associating systems.

It may be seen from Table 2 that the *K* constant not only has no physical meaning but also does not appear to correlate with any behaviour tendency in an homologous series of hydrocarbons or alcohols, possibly because the data used for the calculation originated from various laboratories and were observed at different temperatures. From calculations performed it is evident that *K* should be treated as a third adjustable parameter. Its value can be computed from experimental data in the same way as the two energetic NRTL parameters.

ACKNOWLEDGEMENT

This work was carried out within the Polish Academy of Sciences Research Project WPR 9/111.

REFERENCES

1 P. Gierycz, Thermochim. Acta, 108 (1986) 229.
2 H. Sugi and T. Katayama, J. Chem. Eng. Jpn., 11(3) (1978) 167.
3 P. Oracz, Ph.D. Thesis, Warszawa, 1976.
4 D. Diaz Pena and D. Rodriguez Cheda, An. Quim., 66 (1970) 747.
5 C. Berro, M. Rogalski and A. Peneloux, J. Chem. Eng. Data, 27 (1982) 352.
6 J. Schmelzer, I. Lieberwirth, M. Krug, and R. Pfestorf, Fluid Phase Equilibria, 11 (1983) 187.
7 H.C. Van Ness, C.A. Soczek and N.K. Kochar, J. Chem. Eng. Data, 12 (1967) 346.
8 V.C. Smith and R.L. Robinson, J. Chem. Eng. Data, 15 (1970) 391.

9 T. Treszczanowicz, and A.J. Treszczanowicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 27 (1979) 689.
10 P. Oracz, Methods of Critical Evaluation of VLE Data, Paper presented at CODATA Conference, Paris, 1985.
11 H.V. Kehiaian, and A.J. Treszczanowicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 16 (1968) 445.