

NEW THERMODYNAMIC CONSISTENCY TEST FOR ISOBARIC VAPOUR-LIQUID EQUILIBRIUM DATA

L. Simoiu, I. Trandafir and G. Popescu*

University of Craiova, Faculty of Science, Physical-Chemistry Department A. I. Cuza, 13
1100 Craiova, Romania

Abstract

A thermodynamic consistency test for the vapour-liquid equilibrium data obtained under isobaric conditions is proposed. According to this procedure, the coexistence equation with correction term for the nonideality of the vapour phase was used. The differential equation has two singular points and was solved by numerical integration according to the method predictor-corrector Adams combined with the classical Runge-Kutta method. The nonideality of the vapour phase is considered by using the second coefficients from the virial equation of state. The residuals of the vapour phase obtained as differences between the calculated, respectively experimental values were statistically analysed to detect systematic and random errors. In this order Student and Abbe tests were used. A study of the influence of the method and the step of the integration is also presented. In this order Runge-Kutta and Adams methods were compared and for the estimation of the second virial coefficients different published procedures have been taken into account. In this paper the method of Tsonopoulos and Hayden - O'Connell are taken into account. A correlation analysis is performed to evaluate the results of this study.

Keywords: analysis, equation, method, mixtures, numerical integration, test, thermodynamic consistency, vapour phase, virial coefficient

Introduction

The experience of the fundamentation of many separation processes has shown that in this field both good models and reliable experimental Vapour-Liquid Equilibrium (VLE) data are required. For a good prediction of VLE in multicomponent systems on the basis of the binary measurements, the thermodynamic consistency of the experimental data is a very important condition.

Last years in the literature have been published several methods for checking the thermodynamic consistency (TC) of the VLE data. In this order free model tests, as well as consistency tests takes into account a model have been proposed.

* Author to whom all correspondence should be addressed

An extensive review of the free-model procedures is presented by Dohnal *et al.* [1, 2] and by Kemény *et al.* [3]. Some of their limits are also indicated.

The use of the models for solutions in the consistency tests has as main disadvantage the fact that the results of the analysis of the data could be inexact. The systematic errors of the residuals of the vapour composition, Δy , obtained as deviations from fit models, could be attributed to the inadequacy of the model (Kemény *et al.* [4], Kollár-Hunek *et al.* [5]).

Mathematical model

In this paper a new procedure is developed to check the thermodynamic consistency of the isobaric VLE data. The methods proposed in the literature for the treatment of this kind of data are in many cases semi-empirical, or require explicit information on heat of mixing and have an arbitrary value as acceptance criterion for TC data (Kojima *et al.* [6], Wisniak *et al.* [7]). Unfortunately in the literature experimental excess enthalpy data are still scarce and no reliable methods for their prediction exists.

The proposed method is a model free one and is based on the coexistence equation of the phases under the equilibrium state which has a correction term for the nonideality of the vapour phase. The equation is obtained starting from the general coexistence equation proposed by van Ness and Ljunglin [8].

$$UdP + WdT = (y_1 - x_1)d \ln\left(\frac{\gamma_1^V}{\gamma_2^V}\right) + \frac{y_1 - x_1}{y_1(1 - y_1)}dy_1 \quad (1)$$

where γ is the activity coefficient, x is the composition of the liquid phase, y is the composition of the vapour phase, P is the total pressure and T is the absolute temperature.

In this equation the functions U and W are calculated using the molar heat of mixing, the molar volume change of mixing, respectively, according to the following expressions:

$$W = -(H^{EV} + x_1\bar{H}_1^V + x_2\bar{H}_2^V - H^L)/RT^2 \quad (2)$$

$$U = (V^{EV} + x_1\bar{V}_1^V + x_2\bar{V}_2^V - V^L)/RT \quad (3)$$

where V^{EV} and H^{EV} are respectively, the excess volume and the heat of mixing for the vapour phase.

For isobaric data, dP is 0 and from the Eq. (1) it results:

$$WdT = (y_1 - x_1)d \ln\left(\frac{\gamma_1^V}{\gamma_2^V}\right) + \frac{(y_1 - x_1)}{y_1 y_2}dy_1 \quad (4)$$

where W given by the Eq. (2) represents the change of the molar heat when 1 mol of liquid mixture is evaporated. For low and moderate pressures the function W could be approximated according to the following relation:

$$W = \frac{\Delta H^V}{RT^2} = (z'' - z') \frac{d \ln P}{dT} \quad (5)$$

where z is the compressibility factor for the liquid (z') and for the vapour (z'') phase.

If the temperature dependence of the vapour pressure is given by the Antoine equation:

$$\lg P_i = A_i - B_i / (C_i + t); \quad i = 1, 2 \quad (6)$$

and considering a negligible compressibility factor for the liquid phase as compared to that of the vapour phase the following expression is obtained from the relation (5):

$$W = \frac{\Delta H^V}{RT^2} = 2.303 \left[\frac{B_1 x_1}{(C_1 + t)^2} + \frac{B_2 x_2}{(C_2 + t)^2} \right] \quad (7)$$

where B and C are the Antoine parameters and t is the temperature ($^{\circ}\text{C}$). Combination of Eqs (4) and (7) gives:

$$-2.303 \left[\frac{B_1 x_1}{(C_1 + t)^2} + \frac{B_2 x_2}{(C_2 + t)^2} \right] = (y_1 - x_1) \left[\frac{d \ln(\gamma_1^V / \gamma_2^V)}{dT} + \frac{1}{y_1(1 - y_1)} \frac{dy_1}{dT} \right] \quad (8)$$

For the estimation of the vapour phase composition of the i -th constituent in the vapour phase, y_i it is necessary to know his activity coefficients in the vapour phase, γ_i . The logarithm of the ratio of the activity coefficients in a binary mixture for the vapour phase can be easily estimated according to the relation:

$$\ln \frac{\gamma_1^V}{\gamma_2^V} = \Delta_{12} \frac{P}{RT} (1 - 2y_1) \quad (9)$$

where the parameter Δ_{12} is obtained using the second virial coefficients according to the relation:

$$\Delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (10)$$

On combining the Eqs (8) and (9) and after rearrangements we get:

$$dy_1/dT = W y_1 y_2 / (y_1 - x_1) - y_1 y_2 \left[\frac{d \ln(\gamma_1^V / \gamma_2^V)}{dT} \right] \quad (11)$$

Finally, performing the differentiation with respect to temperature at constant pressure, we obtain the coexistence equation of the phases with correction term for the nonideality of the vapour phase:

$$\frac{dy_1}{dT} = 2.303 \left[\frac{B_1 x_1}{(C_1 + t)^2} + \frac{B_2 x_2}{(C_2 + t)^2} \right] \frac{RT y_1 y_2}{(y_1 - x_1)(RT - 2y_1 y_2 \Delta_{12} P)} - \frac{RT y_1 y_2 P (1 - 2y_1)}{(RT - 2y_1 y_2 \Delta_{12} P)} \left[\frac{d \ln \Delta_{12}}{dT} - \frac{\Delta_{12}}{T} \right] \quad (12)$$

The differential Eq. (12) can be solved by numerical integration and for that it is necessary to know the integration limits. The values dy_1/dT for the extreme composition (to $x_1=0$ and $x_1=1$) are according to l'Hospital's rule:

$$\left(\frac{y_1}{dT} \right)_{x_1 \rightarrow 0} = \left(\frac{\frac{dW}{dT} y_1 y_2}{\frac{d(y_1 - x_1)}{dT}} \right)_{x_1} = \frac{B_2 x_2}{(C_2 + t)^2} + \left(\frac{dx_1}{dT} \right)_{x_1 \rightarrow 0} \quad (13)$$

and

$$\left(\frac{dy_1}{dT} \right)_{x_1 \rightarrow 1} = \left(\frac{dx_1}{dT} \right)_{x_1 \rightarrow 1} = w \quad (14)$$

The values of dx_1/dT necessary in the Eq. (12) for every step of the integration can be obtained taking into account the variation of the boiling temperature with the composition of the liquid phase according to the relation:

$$T(x_1) = A + Bx_1 + Cx_1^2 + Dx_1^3 \quad (15)$$

where the coefficients A , B , C and D are easily obtained by a multiple regression procedure using the experimental measurements of temperatures and the compositions of the liquid phase.

Taking into account the instability of the classical Runge-Kutta method, for the numerical integration of the Eq. (12) the predictor-corrector formulae of Adams [9] was used according to the following relations:

$$y_{n+1}^{(p)} = y_n + \frac{H}{24} (55y_n' - 59y_{n-1}' + 37y_{n-2}' - 9y_{n-3}') \\ y_{n+1}^{(c)} = y_n + \frac{H}{24} (9y_{n+1}' + 19y_n' - 5y_{n-1}' + y_{n-2}') \quad (16)$$

where $y_{n+1}^{(p)}$ is the predicted value and $y_{n+1}^{(c)}$ the corrected value of y_n ; H represents the step of the integration and y' is the derivative dy/dT expressed by the Eq. (12).

The corrector is an implicit formula for y_{n+1} whereas the predictor is derived explicitly. This technique is known as multistep method because more than one previous value of the solution is used in deriving the next value.

The truncated error for the predictor and corrector steps may be derived:

$$\begin{aligned} y_{n+1}^{\text{true}} - y_{n+1}^{(p)} &= 251KH^5/720 \\ y_{n+1}^{\text{true}} - y_{n+1}^{(c)} &= 19KH^5/720 \end{aligned} \quad (17)$$

where K represents the contribution of fifth-order and higher terms, and is assumed to vary little over the interval of integration. Eliminating the term H^5K gives us the following expression:

$$y_{n+1}^{\text{true}} - y_{n+1}^{(p)} - (19/720)(y_{n+1}^{(p)} - y_{n+1}^{(c)}) \quad (18)$$

Thus the truncation error in approximating the integral is directly proportional to the difference between the predicted and corrected values. The estimate for the true value of y_{n+1} may be improved by adding to the corrected value of y_{n+1} the term from the right side of the expression (18). It is possible to do this because the predictor and corrector term are of equal order.

As it can be observed in the multistep predictor-corrector schemes it is necessary to use the results of more than one previous step to calculate y_{n+1} . In order to start the method a Runge-Kutta formula of the same order can be used.

By numerical integration of the Eq. (12) we get the estimated values of the vapour composition of the constituents of the binary mixture.

According to the proposed procedure the residuals, obtained as differences between the estimated and the experimental values of the vapour composition, are statistically analysed. In this order systematic and random errors of the residuals are checked using Student and Abbe tests [11]. The experimental VLE data are considered thermodynamic consistency if there is no shift and no trend in residuals.

There is no shift if the Student parameter, t , is less than the critical value taken for n number of data and for a given significance level. There is no trend in residuals if the Abbe parameter R is larger than the critical value taken, as the Student parameter, for a given significance level and for a specified number of experimental data.

The statistical parameters for Student and Abbe tests have been calculated according to the following relations:

$$t = \frac{\Delta y}{\sqrt{\frac{\sum_i (y_i - \Delta y)^2}{n(n-1)}}} \quad R = \frac{\frac{1}{2(n-1)} \sum_i (\Delta y_{i+1} - \Delta y_i)^2}{\frac{1}{n-1} \sum_i (\Delta y_i - \Delta y)^2} \quad (19)$$

where Δy is the average of all Δy_i ($i=1$ to n number of data).

The factors that can influence the results of the TC analysis according to the proposed procedure

From the analysis of the terms of the Eq. (12) and taken into account the method of the evaluation of the thermodynamic consistency there are considered the following factors that could have some influence on the results of the TC checking of the experimental VLE data:

- the method of the estimation of the second virial coefficients, necessary for the calculation of the correction term for the non-ideality of the vapour phase;
- the method used for the numerical integration of the differential Eq. (12);
- the step of the integration.

All these factors have been studied for the binary mixtures benzene-toluene and cyclohexaneheptane taken from literature [12].

According to the procedures of Herington [13] and Wisniak [7] for both mixtures the data are thermodynamically consistent.

A correlation analysis and Fisher [11] test were used in order to appreciate the influence of the mentioned factors on the results of the TC test using the coexistence equation with correction term for the nonideality of the vapour phase. By correlation analysis it is possible to establish the degree of the dependence of two variables. According to this procedure it is necessary to calculate the determination coefficient using the following relation [11]:

$$r_{x,y}^2 = 1 - s_{y,x}^2/s_y^2 \quad (20)$$

where s^2 represents the variance.

The limiting value for the determination coefficient is 1 indicating a strong influence of the considered variables.

The Fisher test can be used for comparing the results obtained using two different methods. According to Fisher test the null hypothesis is accepted if the following relations is verified:

$$F = s_2^2/s_1^2 < F_{\alpha/2} \quad (21)$$

where α is the confidence interval.

The influence of the method used for the estimation of the second virial coefficients

The term that reflects the nonideality of the vapour phase from the Eq. (12) can be estimated using the parameter Δ_{12} , calculated according to the relation (10). In order to study the influence of the method of the estimation of the virial coefficients the Hayden-O'Connell [14], Tsonopoulos [15] and Vetere [16] correlations have been taken into account.

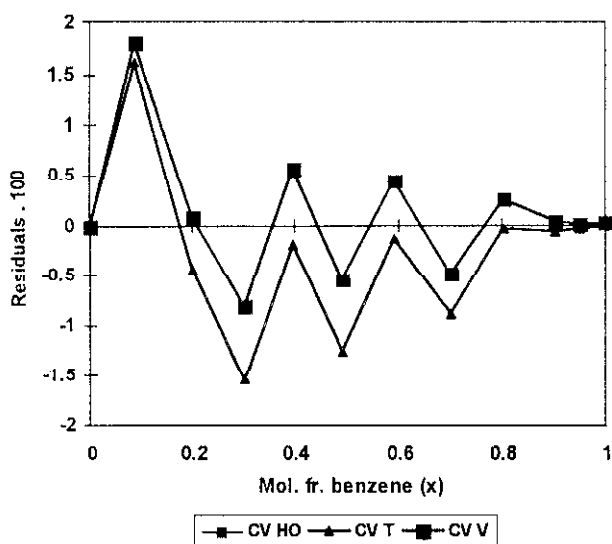


Fig. 1 The residuals of the vapour phase composition in the binary mixtures of benzene with toluene for different virial coefficients correlations; CV HO, CV T, CV V – Hayden-O'Connell, Tsonopoulos and Vetere methods

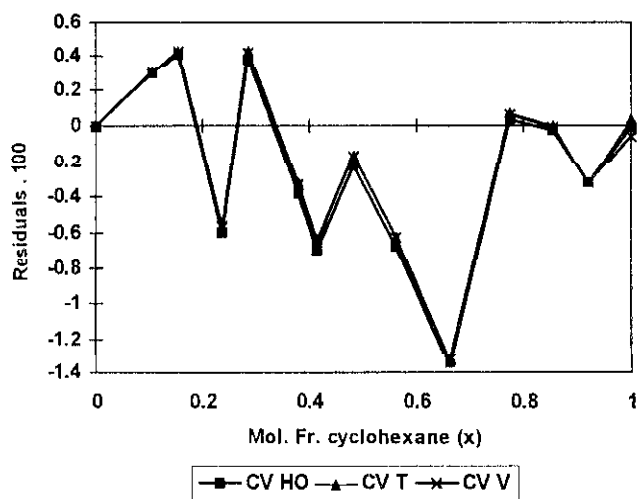


Fig. 2 The residuals of the vapour phase composition in the binary mixtures of benzene with toluene for different virial coefficients correlations; CV HO, CV T, CV V – Hayden-O'Connell, Tsonopoulos and Vetere methods

Using the values of the virial coefficients, for both systems the parameter Δ_{12} has been calculated for every experimental temperatures. By numerical integration of the Eq. (12) the values of the vapour phase composition and the residu-

als are obtained. The plot of the residuals against the experimental composition of the liquid phase, illustrated in Figs 1 and 2, has shown a small differences between the values obtained using the virial coefficients estimated according the methods under consideration.

Table 1 Statistical analysis of the residuals of the vapour phase and the results of the TC test for the system benzene (1)–toluene (2) using different estimation methods of the virial coefficients

Residuals analysis	Hayden-O'Connell	Tsonopoulos	Vetere
Statistical parameters			
$\Delta y 10^3$	1.380	2.960	1.360
$s_{\Delta y} 10^3$	7.360	8.650	7.385
Fisher test, F	$1.003 < F_{cr}=2.297$	$1.179 < F_{cr}=2.297$	$1.007 < F_{cr}=2.297$
TC test			
Student parameter, t	$0.593 < t_{cr}=2.228$	$0.625 < t_{cr}=2.228$	$0.582 < t_{cr}=2.228$
Abbe parameter, R	$0.511 > R_{cr}=0.482$	$0.532 < R_{cr}=0.482$	$0.510 < R_{cr}=0.482$
Shift/trend	—/—	—/—	—/—
Correlation analysis			
coefficient $r_{\Delta y, \Delta_{12}}^2$	0.0034	0.0046	0.0681

Table 2 Statistical analysis of the residuals of the vapour phase and the results of the TC test for the system cyclohexane (1)–heptane (2) using different estimation methods of the virial coefficients

Residuals analysis	Hayden-O'Connell	Tsonopoulos	Vetere
Statistical parameters			
$\Delta y 10^3$	0.263	0.205	0.273
$s_{\Delta y} 10^3$	0.542	0.499	0.456
Fisher test, F	$1.009 < F_{cr}=2.690$	$1.076 < F_{cr}=2.690$	$1.107 < F_{cr}=2.690$
TC test			
Student parameter, t	$1.033 < t_{cr}=2.179$	$1.126 < t_{cr}=2.179$	$1.182 < t_{cr}=2.179$
Abbe parameter, R	$0.544 > R_{cr}=0.447$	$0.530 > R_{cr}=0.447$	$0.532 > R_{cr}=0.447$
Shift/trend	—/—	—/—	—/—
Correlation analysis			
coefficient $r_{\Delta y, \Delta_{12}}^2$	0.0547	0.0586	0.0607

For both mixtures the null hypothesis for Fisher test has been satisfied, indicating no significative influence of the method used for the estimation of the sec-

ond virial coefficients. The results are in good agreement with those obtained for the determination coefficients calculated according to the relation (20). The results of the thermodynamic consistency evaluation of the data, using the proposed procedure, are presented in Table 1 and Table 2 together with the statistical analysis of the residuals. As expected and according to the values of the Student and Abbe tests the thermodynamic consistency of the data are not changed in the case of using different methods for the estimation of the virial coefficients. The presence and the absence of the errors (systematic or random) are indicated by sign '+', respectively '-'. The effect of the cancellation of the errors of method used for the estimation could be a possible explanation of this result.

The influence of the method used for the numerical integration of the coexistence equation

In order to study the influence of the numerical integration method on the results of the TC test classical Runge-Kutta, respectively Adams procedure has been considered. In both cases the second virial coefficients necessary to calculate the parameter Δ_{12} were estimated using the Hayden-O'Connell correlation. The step of the temperature required for the initialisation of the integration of the Eq. (12) was 0.5 C.

In Figs 2 and 3 are shown, for both mixtures, the plot of the residuals of the vapour composition against the mol fractions of benzene, respectively cyclohexane in the liquid phase. As it can be seen there is a large difference between the

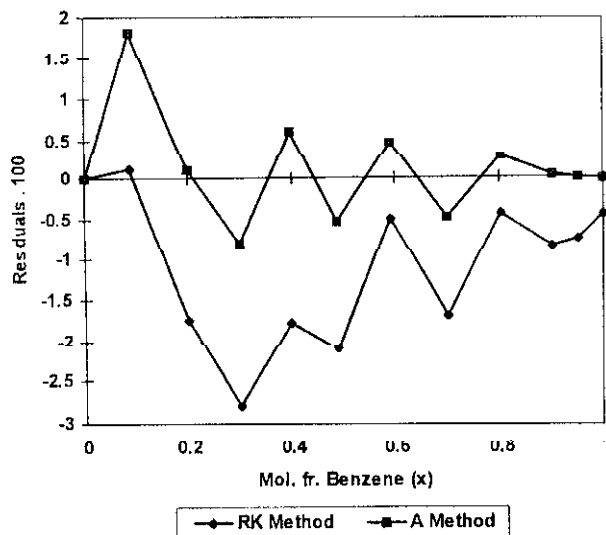


Fig. 3 Residuals of the vapour phase composition in binary system benzene-toluene for different methods of the numerical integration; RK-Runge-Kutta, A-Adams

Table 3 Statistical analysis of the residuals of the vapour phase and the results of the TC test for the systems benzene (1)–toluene (2) and cyclohexane (1)–heptane (2) using different methods of the numerical integration of the coexistence Eq. (12)

Residuals analysis	System benzene–toluene		System cyclohexane–heptane	
	Runge-Kutta	Adams	Runge-Kutta	Adams
Statistical parameters				
$\Delta y 10^3$	10.380	1.381	18.301	0.264
$s_{\Delta y} 10^3$	8.961	7.360	12.603	0.543
Fisher test, F	1.343 < $F_{cr}=2.297$		2.441 < $F_{cr}=2.690$	
TC results				
Student test, t	4.012 > $t_{cr}=2.228$	0.593 < $t_{cr}=2.228$	5.031 > $t_{cr}=2.179$	1.68 < $t_{cr}=2.179$
Abbe test, R	0.907 > $R_{cr}=0.482$	0.511 > $R_{cr}=0.482$	0.644 > $R_{cr}=0.447$	0.54 > $R_{cr}=0.447$
Shift/trend	+/-	/	/	/

values of the residuals obtained using the two methods of integration. The statistical analysis and the results of the TC test are indicated in Table 3. As it can be observed, although the null hypothesis for Fisher test is satisfied in both cases, the results of the TC test indicate inconsistency of the data when Runge-Kutta method is applied for the integration. The parameter Student has exceeded the critical value for the mixtures under consideration and consequently there is shift in the residuals. These results can be explained by the partial instability of the Runge-Kutta method observed earlier by Mayers *et al.* [17]. A numerical solution is considered unstable if, during the development of the algorithm, the numerical value has larger deviations from the real solution. In such cases there is a tendency of the systematisation of the errors which increase in the same time with the increase of the independent variable (the temperature in this case). Another main disadvantage of the Runge-Kutta method is that is not as easy to estimate the accuracy of the procedure.

By comparison, having no partial instability, the predictor-corrector procedures, such as Adams method, offer a better solution of the numerical integration. The accuracy of the results is higher because for every step of the integration there is necessary to pass a convergence test until the predicted and corrected values become equals in the limits of a known errors.

The results of the study have indicated an important influence of the method used for the integration. This influence become greater, especially, when a less precise method is used for the TC evaluation in case of poor quality of the experimental data.

Taken into account the results of this study and theoretical considerations the Adams method is indicated to be used for obtaining the solution of the coexistence Eq. (12).

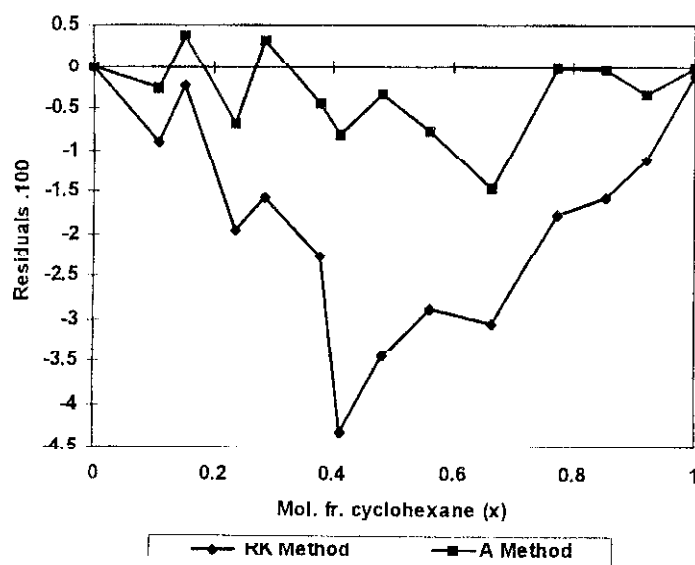


Fig. 4 Residuals of the vapour phase composition in the system cyclohexane-heptane for different methods of the numerical integration; RK-Runge-Kutta, A-Adams

Table 4 Statistical analysis of the residuals of the vapour phase and the results of the TC test for the system benzene (1)-toluene (2) using different integration steps

Integration step/ $^{\circ}\text{C}$	Statistical parameters		Fisher test, F	Results of TC evaluation		
	$\Delta_v 10^3$	$s_{\Delta v} 10^3$		Student, t	Abbe, R	Shift/trend
0.5	1.450	7.335	1.578	0.625	2.129	-/-
0.8	1.183	6.667	1.435	0.615	1.778	-/-
1.0	1.083	6.713	1.445	0.559	2.808	-/-
1.5	1.283	4.646	-	1.554	3.177	-/-
2.0	11.610	17.336	3.371	2.319	1.518	+/-
2.5	11.760	16.889	1.482	2.426	2.058	+/-
3.0	11.492	15.843	3.418	2.314	1.159	+/-
Critical parameters	-	-	2.297	2.228	0.482	-

The influence of the step of the numerical integration

For this study the integration method Adams has been used. The second virial coefficients were estimated according to the Hayden-O'Connell correlation. The

Table 5 Statistical analysis of the residuals of the vapour phase and the results of the TC test for the system cyclohexane (1)–heptane (2) using different integration steps

Integration step/ $^{\circ}\text{C}$	Statistical parameters		Fisher test,	Results of TC evaluation		
	$\Delta y 10^3$	$s_{\text{Av}} 10^3$	F	Student, t	Abbe, R	Shift/trend
0.2	4.107	5.032	1.072	2.099	1.034	-/-
0.5	2.823	4.875	1.038	2.184	1.663	-/-
0.8	3.221	4.693	-	2.568	2.192	+/-
1.0	7.678	9.162	1.953	3.135	2.238	+/-
1.2	0.150	16.237	3.459	3.034	1.642	+/-
1.5	7.735	18.631	3.969	2.553	1.302	+/-
1.8	15.114	26.972	5.747	2.996	0.913	+/-
Critical parameters	-	-	2.690	2.179	0.447	-

results of this study are presented in Tables 4 and 5 and as it can be observed there is an important influence of the step of the integration on the result of the TC test. The thermodynamic inconsistency can be induced when the optimum value of the step of the integration is exceeded. In the case of the Adams method this value is determined by the number of the iterations necessary to assure the convergence. In this way there is the possibility to control the step of the integration and consequently the influence of this factor on the results of the TC test could be negligible.

Conclusions

A free-model procedure for the evaluation of the TC of the isobaric VLE data was developed. The method is based on the coexistence equation of the phase under equilibrium state which has a correction term for the nonideality of the vapour phase. The correction term can be estimated using the parameter Δ_{12} calculated using the second virial coefficients. The procedure doesn't use auxiliaries data such as excess enthalpies which are not very often available in the literature. Also it is not necessary an arbitrary value as acceptance criterion for the TC of the data. The results of the TC analysis are not influenced by the method of the estimation of the virial coefficients. The study of the different integration procedures has indicated the superiority of the predictor-corrector techniques. Having a convergence test, the Adams method has the possibility to control the integration interval and to optimise the step of the integration. The results of the TC analysis are statistically appreciated using Student and Abbe tests.

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