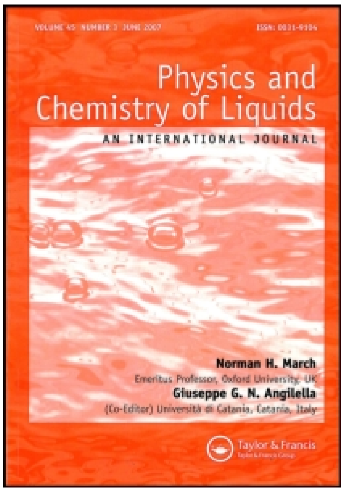

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Experimental data of isobaric vapour-liquid equilibrium for binary mixtures containing tetrahydrofuran and isomeric chlorobutanes

B. Giner[a]; H. Artigas[a]; I. Gascón[a]; P. Cea[a]; F. M. Royo[a]
[a] Departamento de Química Orgánica-Química Física, Facultad de Ciencias, Universidad de Zaragoza, Ciudad Universitaria, 50009 Zaragoza, Spain

To cite this Article Giner, B. , Artigas, H. , Gascón, I. , Cea, P. and Royo, F. M.(2005) 'Experimental data of isobaric vapour-liquid equilibrium for binary mixtures containing tetrahydrofuran and isomeric chlorobutanes', Physics and Chemistry of Liquids, 43: 3, 299 — 307

To link to this Article: DOI: 10.1080/00319100500083872

URL: http://dx.doi.org/10.1080/00319100500083872

Physics and Chemistry of Liquids
Vol. 43, No. 3, June 2005, 299–307

Taylor & Francis
Taylor & Francis Group

Experimental data of isobaric vapour–liquid equilibrium for binary mixtures containing tetrahydrofuran and isomeric chlorobutanes

B. GINER, H. ARTIGAS, I. GASCÓN, P. CEA and F. M. ROYO*

Departamento de Química Orgánica-Química Física, Facultad de Ciencias,
Universidad de Zaragoza, Ciudad Universitaria, 50009 Zaragoza, Spain

(*Received 15 October 2004*)

Isobaric vapour–liquid equilibrium (VLE) measurements for mixtures formed by tetrahydrofuran and isomeric chlorobutanes at 40.0 kPa (except for the mixture containing 2-methyl-2-chloropropane) and 101.3 kPa are reported. The activity coefficients were calculated from experimental data. The mixture containing 2-chlorobutane at 40.0 kPa presents an azeotrope. The VLE measurements have been found thermodynamically consistent according to Van Ness test. Wilson, NRTL, and UNIQUAC equations have been used to correlate the activity coefficients and we have obtained satisfactory results.

Keywords: Tetrahydrofuran; Isomeric chlorobutane; Isobaric VLE

1. Introduction

This article will show part of the results of our systematic study on thermodynamic properties of binary systems containing cyclic ethers and halogenated compounds [1–5]. In previous articles, we have reported experimental data of several thermodynamic properties of these kinds of mixtures and we have obtained very useful information not only about behaviour of mixtures but also of the reliability of estimation methods on these properties. In this case, experimental vapour–liquid equilibrium (VLE) data of mixtures containing tetrahydrofuran and each one of the isomeric chlorobutanes are reported. The measurements were performed under isobaric conditions at pressures of 40.0 and 101.3 kPa, except for 2-methyl-2-chloropropane, which was measured only at 101.03 kPa due to its low boiling temperature. Activity coefficients have been calculated from experimental data and they have been correlated with Wilson [6], NRTL [7], and UNIQUAC [8] equations. Van Ness method [9], described by Fredenslund *et al.* [10], has been used to check thermodynamic consistency of the experimental VLE data. To our knowledge, the VLE data for these mixtures have not been reported before.

---

*Corresponding author. Fax: +34 976 76 12 02. Tel.: + 34 976 761198. Email: femer@unizar.es

Physics and Chemistry of Liquids
ISSN 0031-9104 print: ISSN 1029-0451 online © 2005 Taylor & Francis Group Ltd
DOI: 10.1080/00319100500083872

Table 1. Experimental and literature data of densities, ρ, and normal boiling points, T_b, of pure compounds.

	ρ (kg m^{-3})		T_b (K)	
Compound	Experimental	Literature	Experimental	Literature
Tetrahydrofuran	882.0	881.97[a]	339.12	339.12[b]
1-Chlorobutane	880.7	880.95[b]	351.58	351.58[b]
2-Chlorobutane	867.2	867.1[c]	341.40	341.40[c]
2-Methyl-1-chloropropane	870.9	871.7[b]	342.10	342.0[b]
2-Methyl-2-chloropropane	836.9	836.1[b]	323.83	323.9[b]

[a] Ref. [11].
[b] Ref. [12].
[c] Ref. [13].

Table 2. Experimental VLE data for the systems formed by tetrahydrofuran (1) with isomeric chlorobutane (2) at 40.0 and 101.3 kPa.

T (K)	x_1	y_1	γ_1	γ_2
Tetrahydrofuran (1) + 1-chlorobutane (2) at 40.0 kPa				
323.41	0.0731	0.0997	0.926	1.004
322.49	0.1460	0.1991	0.956	1.003
321.54	0.2296	0.3106	0.982	0.992
320.74	0.2988	0.3969	0.992	0.983
319.94	0.3680	0.4691	0.981	0.990
318.70	0.4699	0.5790	0.992	0.982
317.90	0.5273	0.6400	1.007	0.971
317.31	0.5752	0.6752	0.996	0.998
316.55	0.6445	0.7474	1.012	0.956
315.66	0.7151	0.8001	1.010	0.978
314.84	0.7882	0.8557	1.011	0.981
314.23	0.8535	0.9082	1.015	0.925
313.33	0.9541	0.9689	1.003	1.037
313.44	0.9639	0.9729	0.993	1.144
Tetrahydrofuran (1) + 1-chlorobutane (2) at 101.3 kPa				
350.83	0.0705	0.0879	0.872	1.004
350.43	0.1003	0.1265	0.892	1.005
349.77	0.1645	0.2086	0.914	1.001
348.94	0.2309	0.2971	0.950	0.990
348.05	0.3073	0.3971	0.980	0.970
346.98	0.3766	0.4656	0.968	0.988
346.08	0.4441	0.5414	0.981	0.978
345.47	0.4979	0.5954	0.980	0.974
344.89	0.5399	0.6375	0.985	0.970
343.91	0.6197	0.7124	0.988	0.961
342.53	0.7270	0.8059	0.995	0.945
341.08	0.8215	0.8830	1.009	0.914
340.35	0.8763	0.9149	1.003	0.983
339.53	0.9581	0.9711	1.000	1.013
Tetrahydrofuran (1) + 2-chlorobutane (2) at 40.0 kPa				
314.28	0.1665	0.1675	0.958	0.997
314.28	0.1235	0.1264	0.974	0.995
314.25	0.2746	0.2799	0.972	0.992
314.15	0.3765	0.3833	0.974	0.992
314.12	0.4343	0.4441	0.980	0.987
314.04	0.4949	0.5080	0.986	0.981
313.94	0.5624	0.5775	0.991	0.976
313.85	0.6208	0.6361	0.992	0.973
313.68	0.6984	0.7269	1.014	0.924

(*continued*)

Table 2. Continued.

T (K)	x_1	y_1	γ_1	γ_2
313.65	0.7269	0.7423	0.996	0.964
313.55	0.7841	0.7978	0.996	0.961
313.47	0.8240	0.8367	0.997	0.955
313.21	0.9268	0.9336	0.999	0.943
Tetrahydrofuran (1) + 2-chlorobutane (2) at 101.3 kPa				
341.17	0.0437	0.0446	0.957	1.001
341.10	0.0937	0.0962	0.964	1.001
340.95	0.2156	0.2187	0.958	1.005
340.82	0.3179	0.3288	0.980	0.997
340.78	0.3373	0.3477	0.978	0.998
340.73	0.3628	0.3756	0.984	0.995
340.66	0.3979	0.4118	0.985	0.994
340.54	0.4568	0.4711	0.986	0.995
340.21	0.6049	0.6210	0.992	0.990
340.10	0.6585	0.6760	0.995	0.983
339.99	0.6934	0.7100	0.996	0.983
339.83	0.7602	0.7737	0.995	0.985
339.68	0.8156	0.8281	0.997	0.978
339.51	0.8704	0.8795	0.998	0.981
339.32	0.9254	0.9314	1.000	0.975
Tetrahydrofuran (1) + 2-methyl-1-chloropropane (2) at 40.0 kPa				
315.23	0.1334	0.1369	0.942	0.999
315.08	0.2442	0.2528	0.956	0.997
314.88	0.3559	0.3723	0.974	0.991
314.72	0.4321	0.4527	0.981	0.986
314.52	0.5290	0.5531	0.986	0.978
314.22	0.6381	0.6614	0.989	0.975
314.06	0.6902	0.7161	0.996	0.961
313.81	0.7646	0.7875	0.999	0.956
313.46	0.8785	0.8923	0.998	0.951
313.36	0.9014	0.9126	0.999	0.955
313.27	0.9272	0.9363	1.000	0.946
313.19	0.9490	0.9554	1.000	0.948
313.15	0.9700	0.9732	0.998	0.970
Tetrahydrofuran (1) + 2-methyl-1-chloropropane (2) at 101.3 kPa				
342.04	0.0431	0.0457	0.968	0.999
341.83	0.1291	0.1354	0.963	1.001
341.64	0.2114	0.2221	0.970	1.000
341.30	0.3443	0.3626	0.983	0.996
340.87	0.4900	0.5138	0.992	0.990
340.59	0.5874	0.6102	0.991	0.990
340.25	0.6888	0.7108	0.995	0.984
340.01	0.7648	0.7856	0.998	0.972
339.69	0.8500	0.8620	0.996	0.991
339.43	0.9181	0.9217	0.994	1.038
339.26	0.9644	0.9699	1.001	0.923
Tetrahydrofuran (1) + 2-methyl-2-chloropropane (2) at 101.3 kPa				
324.52	0.0495	0.0282	0.928	1.000
325.49	0.1177	0.0725	0.970	0.997
326.51	0.1945	0.1275	0.997	0.995
327.64	0.2737	0.1867	0.998	0.993
328.10	0.3049	0.2110	0.996	0.993
328.62	0.3392	0.2452	1.022	0.983
329.70	0.4086	0.2983	0.994	0.988
330.47	0.4604	0.3409	0.983	0.994
331.67	0.5361	0.4165	0.990	0.987

(continued)

Table 2. Continued.

T (K)	x_1	y_1	γ_1	γ_2
333.08	0.6309	0.5169	0.996	0.985
334.34	0.7089	0.6091	1.002	0.974
335.51	0.7793	0.6951	1.001	0.968
336.86	0.8671	0.8095	1.003	0.966
338.10	0.9357	0.9060	1.000	0.951

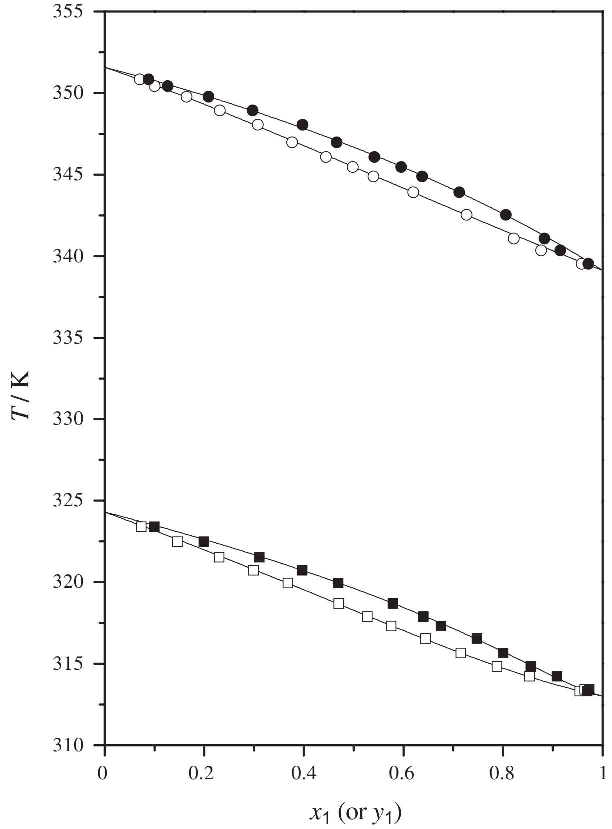

Figure 1. T–x_1–y_1 diagram for tetrahydrofuran (1) + 1-chlorobutane (2): (□,■) experimental data at 40.0 kPa; (○,●) experimental data at 101.3 kPa; and (————) Wilson equation.

2. Experimental

Chemicals used for the determination of VLE were provided by Aldrich (1-chlorobutane and 2-methyl-2-chloropropane have a purity of 99%, tetrahydrofuran and 2-chlorobutane have a purity better than 99.5 and 99%, respectively) and 2-methyl-1-chloropropane was purchased from Fluka (purity better than 98%). Additional purification was not required. A comparison between experimental and literature data of densities at 298.15 K and normal boiling point is reported in table 1 [11–13].

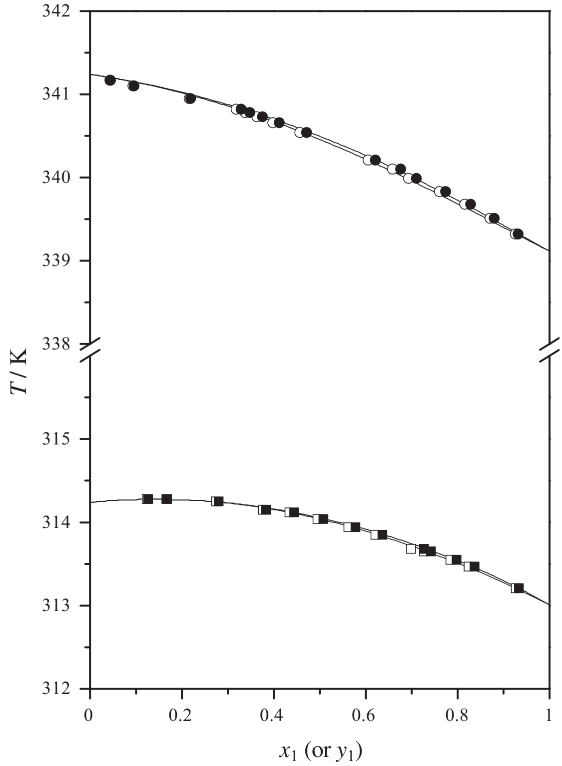

Figure 2. T–x_1–y_1 diagram for tetrahydrofuran (1) + 2-chlorobutane (2): (□,■) experimental data at 40.0 kPa; (○,●) experimental data at 101.3 kPa; and (————) Wilson equation.

Vapour–liquid equilibrium experimental data were measured using a Labodest unit built by Fischer, which is an all-glass dynamic recirculating still equipped with a Cottrell pump, a pressure transducer Druk PDCR 110/W, and a thermometer provided by Automatic System Laboratories (model F25). The accuracy of the thermometer is estimated to be ±0.01 K, while the accuracy of pressure transducer is ±0.1 kPa. Equipment and experimental procedure have been described in a previous article [14]. Composition of both phases has been analysed by density and speed of sound measurements. The error in the determination of liquid and vapour phases is estimated to be ±0.0001. Densities and speeds of sound of the samples were measured by means of an Anton Paar DSA-48 that is able to analyse density and sound simultaneously. Calibration of the analyser was carried out with deionized bidistilled water and dry air. Precision of density measurements was $\pm 3\times10^{-5}\,\mathrm{g\,cm^{-3}}$ and that of the speed of sound measurements was $\pm 1\times10^{-1}\,\mathrm{m\,s^{-1}}$.

3. Results and discussion

The vapour–liquid equilibrium data (T, x_1, and y_1) at 40 and 101.3 kPa along with calculated activity coefficients, γ_i, of components of the studied systems are presented in table 2. Diagrams of temperature–composition are shown in figures 1–4.

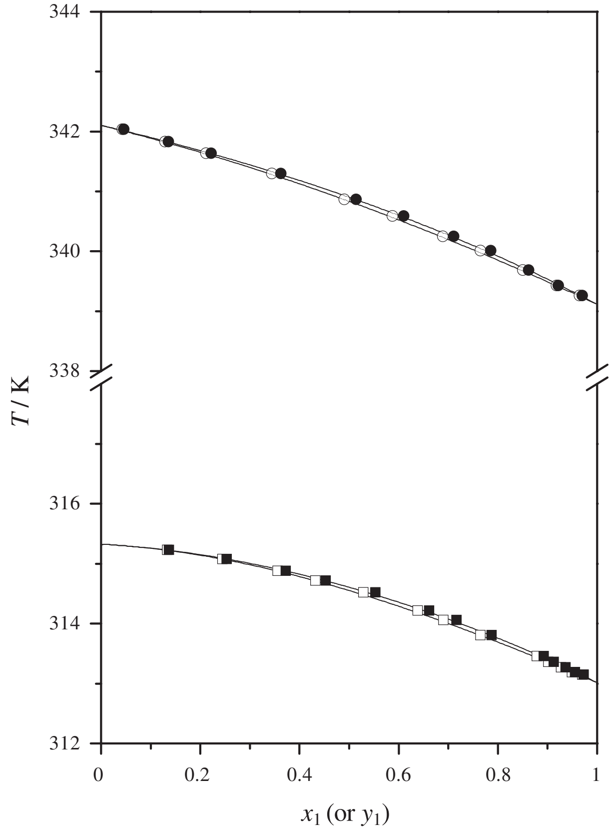

Figure 3. T–x_1–y_1 diagram for tetrahydrofuran (1) + 2-methyl-1-chloropropane (2): (□,■) experimental data at 40.0 kPa; (○,●) experimental data at 101.3 kPa; and (————) Wilson equation.

Activity coefficients γ_i have been calculated using the following equations:

$$\gamma_i = \frac{y_i P}{x_i p_i^0} \exp\left[\frac{(B_{ii} - V_i^0)(P - p_i^0) + (1 - y_i)^2 P \delta_{ij}}{RT}\right] \tag{1}$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \tag{2}$$

where x_i and y_i are the liquid and vapour phase compositions, B_{ii} are the second virial coefficients calculated using the Redlich–Kwong equation [16], and B_{ij} are the cross second virial coefficients calculated using a suitable mixing rule. P is the total pressure, p_i^0 are vapour pressures of the pure compounds calculated from Antoine's equation, where the constants [12,13,15] are given in table 3. V_i^0 is the molar volume of saturated pure liquid, which was calculated from Yen and Woods method [17]. The exponential term in equation (1) is considered important only at diluted solutions.

Activity coefficients were correlated with Wilson, NRTL, and UNIQUAC equations. The mixture non-randomness parameter, α_{12}, in the NRTL equation was taken as 0.3

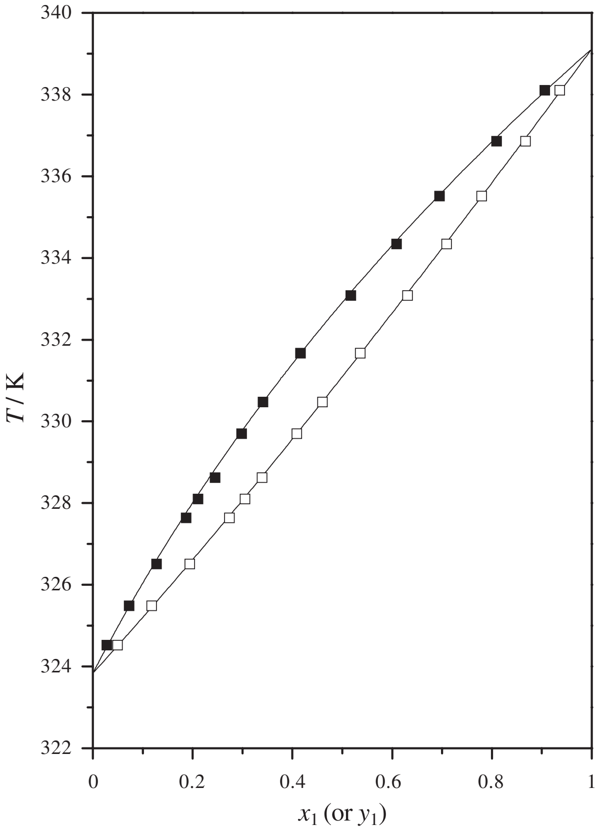

Figure 4. T–x_1–y_1 diagram for tetrahydrofuran (1) + 2-methyl-2-chloropropane (2): (□, ■) experimental data at 101.3 kPa and (————) Wilson equation.

for all the systems. Estimation of the equations was based on minimization using the Simplex method [18] of the following objective function:

$$F = \sum_{k=1}^{N} \sum_{i=1}^{2} \left(\frac{\gamma_i^{\text{exptl}} - \gamma_i^{\text{cal}}}{\gamma_i^{\text{exptl}}} \right)^2 \tag{3}$$

where N is the number of experimental data points. This was formulated by Silvermann and Tassios [19].

Adjustable parameters A_{ij} for the coefficient activity equations, which are defined in [15], along with average deviations in temperature, ΔT, vapour phase composition, Δy, and activity coefficients at infinite dilution, γ_i^{∞} are given in table 4. The average deviation values for temperature are between 0.01 K and 0.13 K and the average deviations for vapour composition lie between 0.0008 and 0.0041. It can be asserted that all the equations show a good performance in correlating the activity coefficients. Wilson equation has been used to obtain the T–x_1–y_1 diagrams, which are shown for all the mixtures at 101.13 and 40.0 kPa in figures 1–4 together with the experimental data.

Table 3. Coefficients of Antoine's equation for the pure compounds (temperature in °C and pressure in kPa).

Compound	*A*	*B*	*C*
Tetrahydrofuran[a]	6.12142	1203.11	226.355
1-Chlorobutane[b]	6.05154	1216.82	222.33
2-Chlorobutane[b]	6.1222	1245.2	234.4
2-Methyl-1-chloropropane[c]	6.01854	1176.06	224.125
2-Methyl-2-chloropropane[c]	5.99201	1114.899	229

[a] Ref. [12].
[b] Ref. [13].
[c] Ref. [15].

Table 4. Correlation parameters, A_{ij}, average deviations, ΔT and Δy, and activity coefficients at infinite dilution, γ_i^∞, of the studied mixtures.

Equation	A_{12} (J mol^{-1})	A_{21} (J mol^{-1})	ΔT (K)	Δy	γ_1^∞	γ_2^∞
Tetrahydrofuran (1) + 1-chlorobutane (2) at 40.0 kPa						
Wilson	−1643.2533	3477.1939	0.05	0.0031	0.93	1.20
NRTL	−533.1274	501.4537	0.13	0.0040	0.98	0.98
UNIQUAC	−329.2618	319.3920	0.13	0.0041	0.98	0.98
Tetrahydrofuran (1) + 1-chlorobutane (2) at 101.3 kPa						
Wilson	1757.8404	−1833.5928	0.08	0.0027	0.90	0.93
NRTL	−1255.3554	1132.3994	0.08	0.0029	0.90	0.91
UNIQUAC	−674.7561	648.6183	0.09	0.0033	0.91	0.91
Tetrahydrofuran (1) + 2-chlorobutane (2) at 40.0 kPa						
Wilson	727.6585	−896.8372	0.01	0.0018	0.93	0.94
NRTL	−256.4726	87.5535	0.01	0.0019	0.93	0.94
UNIQUAC	−877.8290	976.2534	0.01	0.0019	0.94	0.94
Tetrahydrofuran (1) + 2-chlorobutane (2) at 101.3 kPa						
Wilson	1376.2564	−1415.0718	0.02	0.0012	0.96	0.96
NRTL	−797.5168	749.3097	0.02	0.0011	0.96	0.96
UNIQUAC	−494.0679	485.5779	0.02	0.0011	0.96	0.96
Tetrahydrofuran (1) + 2-methyl-1-chloropropane (2) at 40.0 kPa						
Wilson	1567.0763	−1585.3781	0.01	0.0008	0.93	0.94
NRTL	−981.1719	917.7638	0.02	0.0008	0.93	0.94
UNIQUAC	−664.2019	657.8363	0.02	0.0008	0.93	0.94
Tetrahydrofuran (1) + 2-methyl-1-chloropropane (2) at 101.3 kPa						
Wilson	825.8188	−922.7242	0.01	0.0015	0.96	0.97
NRTL	−348.4627	258.0052	0.01	0.0015	0.96	0.97
UNIQUAC	−122.0926	53.8439	0.01	0.0015	0.97	0.97
Tetrahydrofuran (1) + 2-methyl-2-chloropropane (2) at 101.3 kPa						
Wilson	−596.6592	948.2982	0.03	0.0024	0.96	0.97
NRTL	−813.6012	764.2991	0.03	0.0024	0.95	0.96
UNIQUAC	−376.0335	370.5092	0.03	0.0024	0.96	0.96

The mixture formed by tetrahydrofuran and 2-chlorobutane at 40 kPa presents an azeotrope at $x_1 = 0.1460$ and at $T = 314.30$ K.

At both pressures, systems present slightly positive deviations from ideal behaviour. It is significant that almost all activity coefficients are close to 1. This might be due to the compensation of opposite effects during the mixture process – the weakening of dipole–dipole interactions in the pure compounds on one hand and new interactions formed between chlorine and oxygen atoms on the other.

Thermodynamic consistency of the experimental results has been checked using Van Ness method, described by Fredenslund. According to this method, experimental

Table 5. Results of thermodynamic consistence test. Average deviations of ΔP and Δy.

Mixture	P (kPa)	ΔP (kPa)	Δy
Tetrahydrofuran + 1-chlorobutane	40.0	0.1	0.0030
	101.3	0.4	0.0034
2-Chlorobutane	40.0	0.0	0.0023
	101.3	0.1	0.0013
2-Methyl-1-chloropropane	40.0	0.0	0.0006
	101.3	0.2	0.0020
2-Methyl-2-chloropropane	101.3	0.3	0.0021

data are supposed to be thermodynamically consistent if mean absolute deviation between calculated and measured vapour phase compositions, Δy, is lower than 0.01. According to this, all the studied mixtures are thermodynamically consistent and values of ΔP and Δy are shown in table 5.

Acknowledgement

The authors are grateful for the financial assistance from Ministerio de Ciencia Y Tecnología. Proyecto BQU 2003-01765.

References

[1] A. Reyes, M. Haro, I. Gascón, H. Artigas, C. Lafuente, *J. Chem. Eng. Data*, **48**, 887 (2003).
[2] B. Giner, M.E. Aldea, S. Martín, I. Gascón, C. Lafuente, *J. Chem. Eng. Data*, **48**, 1296 (2003).
[3] A. Valen, I. Gascón, C. Lafuente, M.C. López, F.M. Royo, *Phys. Chem. Liq.*, **41**, 239 (2003).
[4] I. Gascón, S. Martín, B. Giner, M. Haro, C. Lafuente, *Can. J. Chem.*, **81**, 357 (2003).
[5] S. Rodríguez, C. Lafuente, P. Cea, M.C. López, F.M. Royo, *Phys. Chem. Liq.*, **40**, 715 (2002).
[6] G.M. Wilson, *J. Am. Chem. Soc.*, **86**, 127 (1964).
[7] N. Renon, J.M. Prausnitz, *AIChE J.*, **14**, 299 (1967).
[8] D.S. Abrams, J.M. Prausnitz, *AIChE J.*, **21**, 116 (1975).
[9] H.C. Van Ness, S.M. Byer, R.E. Gibbs, *AIChE J.*, **19**, 238 (1973).
[10] A. Fredenslund, J. Gmehling, P. Rasmusen, *Vapour-Liquid Equilibria Using Unifac*, Elsevier, Amsterdam (1977).
[11] O. Kiyohara, P.J. D'Arcy, G. Benson, *Can. J. Chem.*, **57**, 1006 (1979).
[12] TRC Tables, *Selected Values of Properties of Chemical Compounds, Thermodynamic Research Center Data Project*, p. a-7040, a-6170, k-6170, Texas A&M University, College Station, TX (1983).
[13] J.A. Riddick, W.B Bunger, T.K. Sanako, *Organic Solvents. Physical Properties and Methods of Purification* (*Techniques of Chemistry*), 4th Edn, pp. 471–475, Wiley Interscience, New York (1986).
[14] H. Artigas, C. Lafuente, M.C. López, F.M. Royo, J.S. Urieta, *J. Chem. Eng. Data*, **39**, 729 (1994).
[15] J. Gmehling, U. Onken, W. Arlt, *Vapour–Liquid Equilibrium Data Collection DECHEMA Chemistry Data Series*, Vol. I, Part 8, Frankfurt/Main pp. xl–xli (1981).
[16] O. Redlich, J.N.S. Kwong, *Chem. Rev.*, **44**, 233 (1949).
[17] L.C. Yen, S.S. Woods, *AIChE J.*, **14**, 95 (1968).
[18] J.A. Nelder, R.A. Mead, *Comput. J.*, **7**, 308 (1965).
[19] N. Silvermann, P.D. Tassios, *Ind. Eng. Chem. Process. Des. Dev.*, **23**, 586 (1984).