Thermochimica Acta 484 (2009) 22–26

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Experimental and predicted viscosities of binary mixtures of cyclic ethers with 1-chloropentane or 1-chlorohexane at 283.15, 298.15, and 313.15 K

Isabel Bandrés, Ignacio Giner, M. Eugenia Aldea, Pilar Cea, Carlos Lafuente*

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

ARTICLE INFO

Article history:
Received 4 July 2008
Received in revised form 6 October 2008
Accepted 25 November 2008
Available online 3 December 2008

Keywords:
Cyclic ether
Chloroalkane
Viscosities
Asfour-method

ABSTRACT

Viscosities for the binary mixtures of tetrahydrofuran, tetrahydropyran, 1,3-dioxolane or 1,4-dioxane with 1-chloropentane or 1-chlorohexane have been determined at 283.15, 298.15 and 313.15 K, except for the mixtures containing 1,4-dioxane whose measurements were carried out only at 298.15 and 313.15 K. Kinematic viscosities have been correlated by the McAllister equation. Viscosity deviations have been calculated from viscosity data for all the mixtures and results have been fitted with the Redlich–Kister equation. Experimental values of kinematic viscosity have been compared to values predicted by means of the Asfour method.

1. Introduction

The knowledge of viscosity is an essential requirement in the design of different industrial processes due to their importance in heat and mass transfer calculations. Moreover, since this property seems to be determined by several factors such as the size and shape of the molecules and the intermolecular interactions, important theoretical information on the structure and interactions of liquids can be obtained from experimental data of viscosity. For these reasons, a great effort has been made to obtain data of this transport property in order to characterize different mixtures.

During the last years, our research group has studied thermodynamic and transport properties of binary liquid mixtures containing a cyclic ether and isomeric chlorobutanes [1–5]. In order to extend and complete this work to other chloroalkanes [6,7], in this paper we report dynamic viscosities of mixtures containing some cyclic ethers such as tetrahydrofuran, tetrahydropyran, 1,3-dioxolane, and 1,4-dioxane and several chloroalkanes such as 1-chloropentane, and 1-chlorohexane at temperatures of 283.15, 298.15, and 313.15 K, except for the mixtures formed by 1,4-dioxane, whose measurements were carried out only at 298.15 and 313.15 K. Kinematic viscosities have been correlated using the McAllister equation [8] and viscosity deviations have been fitted by means of the Redlich–Kister equation. After the revision of literature, we have found just a previous reference of viscosities of the binary mixture 1,4-dioxane + 1-chorohexane at 303.15 K [9].

These mixtures have a great interest since new donor–acceptor type interactions can be formed between the unlike molecules due to the presence of the ether and the halogen groups in the studied compounds. Moreover, polar interactions in pure chemicals are supposed to be debilitated during the process mixture. Viscosity deviations from linearity provide important information about these effects that can take place in the process mixture. For this reason, the analysis of the obtained results can be interpreted in terms of resultant behaviour of the studied binary mixtures.

Because of experimental data of this transport property are not always available and taking into account their practical and theoretical importance, several methods have been proposed to predict viscosities of liquid mixtures [10–13], being experimental data essential to the development of new accurate predictive models. The Asfour method [10,11] predicts the McAllister viscosity model parameters from pure component properties for binary liquid systems. In this work we have compared our experimental values with those estimated by the Asfour method in order to evaluate the suitability of this model in the prediction of kinematic viscosities.

2. Experimental

The used compounds tetrahydrofuran (99.5%), 1,3-dioxolane (99%), 1-chloropentane (99%), and 1-chlorohexane (99%), were obtained from Aldrich, while tetrahydropyran (99%), was supplied by Across, and 1,4-dioxane (≥99.5%) was obtained from Fluka. No additional purification has been carried out.

Kinematic viscosities, ν, were determined using an Ubbelohde viscosimeter with a Schoot-Geräte automatic measuring unit model

---

* Corresponding author.
E-mail address: celadi@unizar.es (C. Lafuente).

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.11.009

AVS-440, being the measuring range of 0.5–3 $mm^2 s^{-1}$. The temperature was kept constant within ±0.01 K by means of a Schoot-Geräte thermostat. The temperature in the bath was controlled using a thermometer model F25 with a PT100 probe calibrated according to ITS-90 from Automatic Systems Laboratories. The viscosimeter was calibrated with deionised doubly distilled water. At least four time flow measurements were performed for each composition and temperature, and the results were averaged. Kinetic energy corrections were applied to the experimental data. The uncertainty of the time flow measurements was ±0.01 s, and the corresponding uncertainty in the kinematic viscosity was $\pm 1 \times 10^{-4}$ $mm^2 s^{-1}$.

Densities, ρ, required for calculate dynamic viscosities from kinematic viscosities ($\eta = \rho \times \nu$), were measured using an Anton Paar DMA-58 vibrating tube densimeter in which temperature is internally controlled at ±0.01 K by means of a Peltier device calibrated according to ITS-90. The apparatus was calibrated with deionised doubly distilled water and dry air. The uncertainty of the density measurements was $\pm 1 \times 10^{-5}$ g cm^{-3}.

The viscosity and density values of the pure components appear together with their corresponding literature values at 298.15 K in Table 1.

The mixtures were prepared using a Sartorious semi-micro balance CP225-D with an uncertainty of $\pm 10^{-5}$ g. The maximum estimated error in the mole fraction is $\pm 1 \times 10^{-4}$.

3. Results and discussion

Kinematic, ν, and dynamic viscosities, η, for the liquid binary mixtures at the studied temperature are collected in Supplementary Material.

The kinematic viscosity data were correlated by using the McAllister [8] equation:

$$\begin{aligned}\ln \nu = {} & x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 \\ & - \ln[x_1 + x_2 M_2/M_1] + 3x_1^2 x_2 \ln[(2 + M_2/M_1)/3] \\ & + 3x_1 x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \end{aligned} \tag{1}$$

where ν refers to the kinematic viscosity of the mixture, ν_1 and ν_2 are the kinematic viscosities of components 1 and 2, M_1 and M_2 are their corresponding molecular masses and ν_{12} and ν_{21} are adjustable parameters characteristic of the system.

The estimated parameters of McAllister equation and the corresponding mean relative square deviation (MRSD) between experimental and correlated values are shown in Table 2. At the light of the MRSD values, being in all cases less than 0.2%, we can conclude that McAllister equation correlates with good quality the kinematic viscosity data.

Viscosity deviations, $\Delta\eta$, have been calculated from experimental values by means the following equation:

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{2}$$

The calculated values of viscosity deviations are reported in the Supplementary Material and they are represented in Figs. 1 to 4.

Experimental values of viscosity deviations have been fitted to a Redlich–Kister equation:

$$\Delta\eta = x_1(1 - x_1)\sum_{i=0}^{i=n} A_i(2x_1 - 1)^i \tag{3}$$

where A_i are adjustable parameters obtained by the least-squares method. Their values are given together with standard deviations, σ, in Table 3.

Viscosity deviation values are negative for the studied binary mixtures in whole composition range at all the temperatures, excepting for mixtures containing tetrahydrofuran. In this case the behaviour is quite different since viscosity deviations in absolute values are bigger when mixture is formed by 1-chlorohexane while for the other mixtures, containing tetrahydropyran, 1,3-dioxolane, or 1,4-dioxane and 1-chloropentane, viscosity deviations are bigger. If we compare these experimental data with previous results for the mixtures cyclic ether + 1-chlorobutane [1–3], we can see a systematic variation of viscosity deviations with the length of the alkyl chain of the chloroalkane. That is, when the length of the chloroalkane increases, viscosity deviations in absolute value increase when mixtures are constituted by tetrahydrofuran, while deviations decrease for the mixtures formed by tetrahydropyran, 1,3-dioxolane, and 1,4-dioxane. For a given halogenated compound, it is noticeable that viscosity deviations in absolute value for 1,4-dioxane mixtures are larger than those for the rest of the stud-

Table 1
Densities, ρ, and viscosities, η, of pure compounds at 298.15 K and comparison with literature data.

Compound	ρ (g cm^{-3})		η (mPa s)	
	Exp.	Lit.	Exp.	Lit.
Tetrahydrofuran	0.88195	0.8825[a]	0.4631	0.456[a]
Tetrahydropyran	0.87881	0.87916[b]	0.7997	0.764[c]
1,3-Dioxolane	1.05862	1.05866[d]	0.5882	0.531[e]
1,4-Dioxane	1.02787	1.02797[f]	1.1807	1.181[g]
1-Chloropentane	0.87700	0.8771[a]	0.5507	0.5461[f]
1-Chlorohexane	0.87356	0.87354[h]	0.6943	0.7173[i]

[a] Ref. [14].
[b] Ref. [15].
[c] Ref. [19].
[d] Ref. [16].
[e] Ref. [20].
[f] Ref. [17].
[g] Ref. [21].
[h] Ref. [18].
[i] Ref. [22].

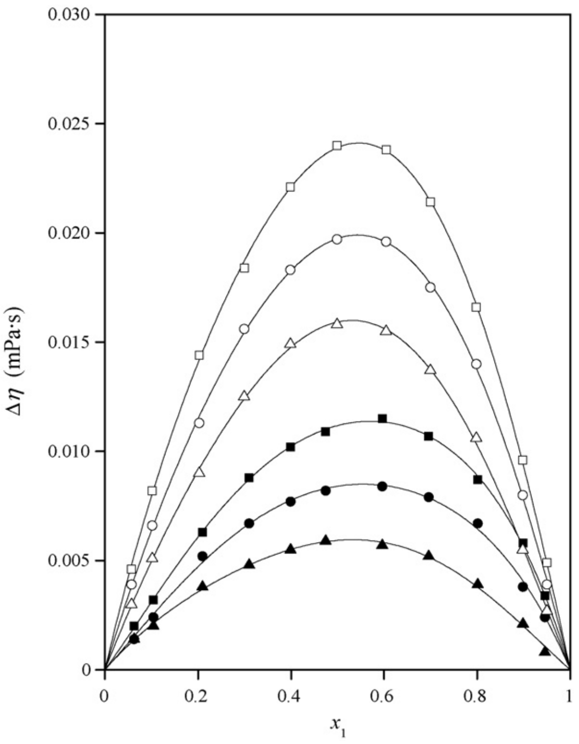

Fig. 1. Viscosity deviations, $\Delta\eta$, of mixtures tetrahydrofuran (1) + 1-chloropentane (2) at 283.15 K (■), 298.15 K (●), and 313.15 K (▲) or 1-chlorohexane (2) at 283.15 K (□), 298.15 K (○), and 313.15 K (△).

Table 2

Parameters of the McAllister equation and the Asfour method with their corresponding mean relative square deviation, MRSD.

System	T (K)	McAllister equation			Asfour method		
		ν_{12}	ν_{21}	MRSD %	ν_{12}	ν_{21}	MRSD %
Tetrahydrofuran+							
1-Chloropentane	283.15	0.6811	0.7059	0.06	0.6157	0.6550	4.67
	298.15	0.5843	0.6070	0.05	0.5308	0.5634	4.54
	313.15	0.5038	0.5267	0.03	0.4626	0.4887	4.29
1-Chlorohexane	283.15	0.7954	0.8739	0.07	0.7334	0.8505	3.70
	298.15	0.6761	0.7380	0.06	0.6274	0.7204	3.42
	313.15	0.5799	0.6329	0.04	0.5442	0.6190	3.11
Tetrahydropyran+							
1-Chloropentane	283.15	0.8781	0.8046	0.10	0.8501	0.7375	3.85
	298.15	0.7382	0.6818	0.12	0.7032	0.6291	3.85
	313.15	0.6319	0.5852	0.08	0.5923	0.5299	4.63
1-Chlorohexane	283.15	1.0016	0.9896	0.15	0.9495	0.8980	3.94
	298.15	0.8329	0.8234	0.08	0.7794	0.7507	4.12
	313.15	0.7054	0.6978	0.08	0.6534	0.6294	4.64
1,3-Dioxolane+							
1-Chloropentane	283.15	0.6732	0.6927	0.06	0.6346	0.6591	2.88
	298.15	0.5716	0.5937	0.06	0.5417	0.5641	2.81
	313.15	0.4917	0.5111	0.04	0.4667	0.4866	2.74
1-Chlorohexane	283.15	0.7866	0.8578	0.03	0.7504	0.8497	2.59
	298.15	0.6670	0.7235	0.06	0.6357	0.7162	2.51
	313.15	0.5735	0.6178	0.07	0.5451	0.6119	2.47
1,4-Dioxane+							
1-Chloropentane	298.15	0.7558	0.6888	0.01	0.8220	0.6721	3.51
	313.15	0.7047	0.5892	0.05	0.6750	0.5659	4.19
1-Chlorohexane	298.15	0.8486	0.8384	0.20	0.8932	0.7900	1.44
	313.15	0.7107	0.7059	0.18	0.7301	0.6590	1.57

Table 3

Parameters, A_i, and standard deviations, σ, for the Redlich–Kister equation.

Compound	T (K)	A_0	A_1	A_2	A_3	σ
Tetrahydrofuran+						
1-Chloropentane	283.15	0.0439	0.0116	0.0043	0.0082	0.0003
	298.15	0.0336	0.0067	0.0036	0.0065	0.0002
	313.15	0.0234	0.0038	−0.0019	−0.0064	0.0002
1-Chlorohexane	283.15	0.0956	0.0154	−0.0016	−0.0098	0.0002
	298.15	0.0790	0.0143	−0.0007	−0.0075	0.0002
	313.15	0.0637	0.0092	−0.0088	−0.0088	0.0002
Tetrahydropyran+						
1-Chloropentane	283.15	−0.2511	−0.1079	−0.0480	−0.0099	0.0002
	298.15	−0.1711	−0.0691	−0.0406	−0.0126	0.0003
	313.15	−0.1181	−0.0431	−0.0206	−0.0095	0.0002
1-Chlorohexane	283.15	−0.1214	−0.0819	−0.0493	0.0110	0.0002
	298.15	−0.0798	−0.0447	−0.0235	−0.0118	0.0002
	313.15	−0.0522	−0.0298	−0.0170	−0.0058	0.0002
1,3-Dioxolane+						
1-Chloropentane	283.15	−0.1047	−0.0170	−0.0119	0.0121	0.0004
	298.15	−0.0907	−0.0179	−0.0119	0.0048	0.0004
	313.15	−0.0810	−0.0185	−0.0037	0.0094	0.0002
1-Chlorohexane	283.15	−0.0395	0.0055	−0.0062	−0.0032	0.0002
	298.15	−0.0300	0.0021	−0.0001	0.0025	0.0002
	313.15	−0.0233	0.0030	0.0033	0.0011	0.0002
1,4-Dioxane+						
1-Chloropentane	298.15	−0.6516	−0.3093	−0.1157	−0.0450	0.0002
	313.15	−0.3713	−0.0956	−0.0187	−0.0018	0.0003
1-Chlorohexane	298.15	−0.5267	−0.2361	−0.1024	−0.1276	0.0011
	313.15	−0.3722	−0.1616	−0.0583	−0.0807	0.0011

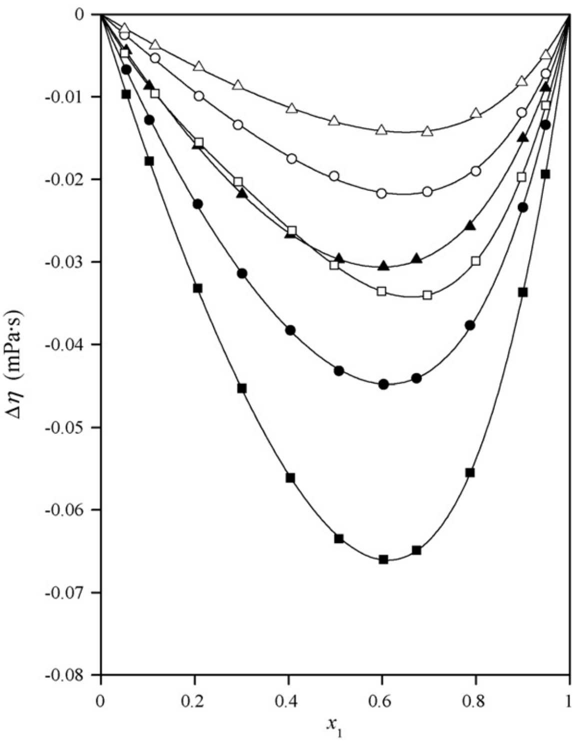

Fig. 2. Viscosity deviations, $\Delta\eta$, of mixtures tetrahydropyran (1) + 1-chloropentane (2) at 283.15 K (■), 298.15 K (●), and 313.15 K (▲) or 1-chlorohexane (2) at 283.15 K (□), 298.15 K (○), and 313.15 K (△).

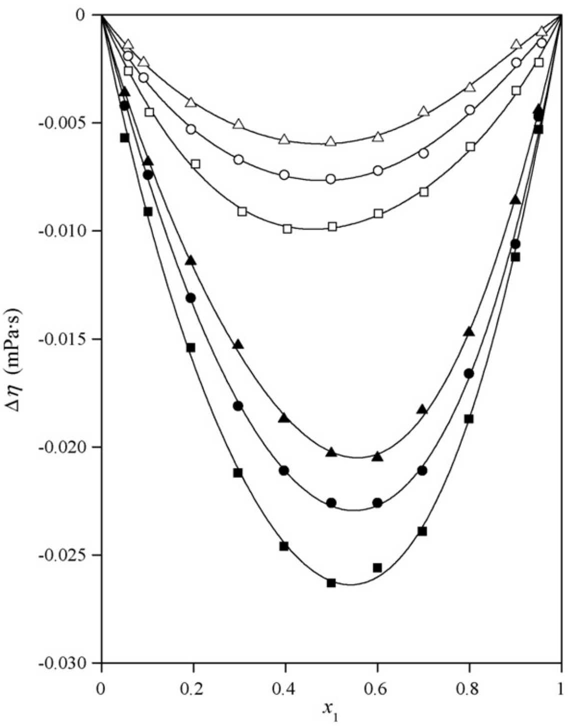

Fig. 3. Viscosity deviations, $\Delta\eta$, of mixtures 1,3-dioxolane (1) + 1-chloropentane (2) at 283.15 K (■), 298.15 K (●), and 313.15 K (▲) or 1-chlorohexane (2) at 283.15 K (□), 298.15 K (○), and 313.15 K (△).

ied systems. The maximum viscosity deviation in absolute value in mixtures tetrahydrofuran + 1-chlorohexane, 1,3-dioxolane + 1-chloropentane, and 1,3-dioxolane + 1-chlorohexane appears near the equimolecular composition. On the other hand, the rest of systems are slightly shifted toward rich compositions in cyclic ether. The effect of temperature in viscosity deviations is similar in all the systems; the property in absolute value increases somewhat when temperature decreases.

Results can be analysed taking into account energetic factors which take place during the mixture process. As we have mentioned before, the most important effects in these kind of mixtures are in one hand, the weakness or the breaking of interactions in pure compounds due to the presence of the other component and on the other hand, the formation of new interactions between unlike molecules. The smaller values of deviations for tetrahydrofuran, tetrahydropyran, and 1,3-dioxolane mixtures seem to be a consequence of counterbalance of both opposite effects. That is, the disrupt of interactions in pure compounds are compensated by new donor–acceptor ether–haloalkane interactions. On the other hand, negative values for 1,4-dioxane suggest that polar interactions of compounds are weakened in the process mixture, predominating over the new interactions between the oxygen atom of the ether and the chlorine atom of the halogenated compound.

4. Asfour method

McAllister equation [8], which is based on Eyring's absolute rate theory, is considered as one of the best available correlative method for the dependence of kinematic viscosity on composition [11]. As we have mentioned before, the model contains two adjustable parameters, ν_{12} and ν_{21}, which are determinate by fitting experimental kinematic viscosity-composition data to the Eq. (1). The presence of such parameters makes that this model can be considerate only as a correlation method. The Asfour method [10,11] was proposed with the aim of using McAllister equation as a predictive model. It is based on the effective carbon number for estimating the McAllister model interaction parameters from pure component and molecular properties for liquid binary mixtures, making possi-

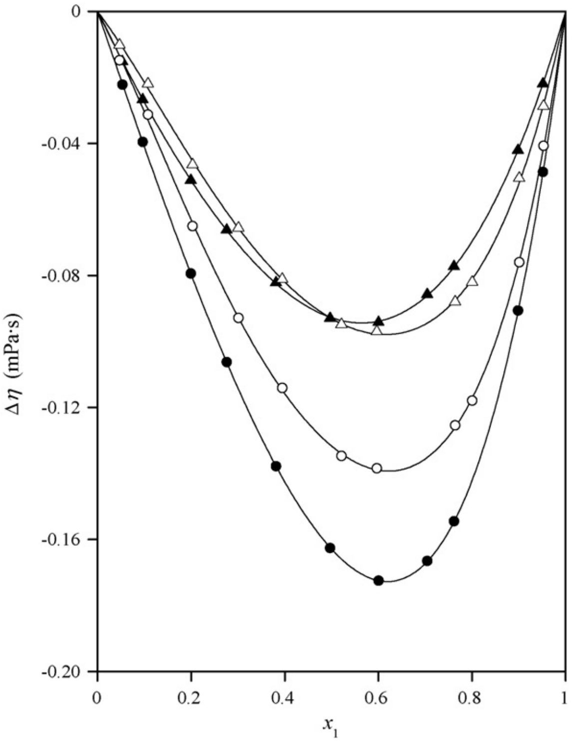

Fig. 4. Viscosity deviations, $\Delta\eta$, of mixtures 1,4-dioxane (1) + 1-chloropentane (2) at 298.15 K (●), and 313.15 K (▲) or 1-chlorohexane (2) at 298.15 K (○), and 313.15 K (△).

Table 4
Experimental kinematic viscosities at 308.15 K and effective carbon number, *N*, for pure compounds.

Compound	ν (mm^2 s)	N
Tetrahydrofuran	0.4749	4.66
Tetrahydropyran	0.8197	6.78
1,3-Dioxolane	0.5045	4.89
1,4-Dioxane	0.9884	7.51
1-Chloropentane	0.5626	7.09
1-Chlorohexane	0.7095	8.29

ble to predict the dependence of viscosity on composition over the entire composition range. In order to evaluate the suitability of this method, in this work experimental data have been compared with viscosity prediction values for the studied binary mixtures.

The effective carbon number, *N*, is an intrinsic property of each compound which can be calculated from the kinematic viscosity of the pure components at the temperature of 308.15 K using the following equation:

$$\ln\ \nu = -1.943 + 0.193N \tag{4}$$

Asfour and coworkers [23] reported that this equation tends to overpredict the effective carbon number of cyclic compounds, so better estimations are obtained for this type of chemicals multiplying by 0.75 the calculated value using Eq. (4). The kinematic viscosity at 308.15 K and the effective carbon number values for the studied compounds taking into account these considerations are collected in Table 4.

Then, the McAllister model interaction parameters can be calculated, for regular solutions, by means of these expressions:

$$\frac{\nu_{AB}}{(\nu_A^2\nu_B)^{1/3}} = 0.8735 + 0.0715\frac{(N_B - N_A)^2}{(N_A^2 N_B)^{1/3}} \tag{5}$$

$$\nu_{BA} = \nu_{AB}\left(\frac{\nu_B}{\nu_A}\right)^{1/3} \tag{6}$$

Kinematic viscosity can be estimated once the values of the parameters have been obtained. In order to evaluate the agreement between experimental and estimated values, the mean relative square deviation (MRSD) expressed in % have been calculated using the following equation:

$$\mathrm{MRSD} = 100\left(\frac{1}{m}\sum_{i=1}^{m}\left(\frac{\nu_{i,\mathrm{exp}} - \nu_{i,\mathrm{Asfour}}}{\nu_{i,\mathrm{exp}}}\right)^2\right)^{1/2} \tag{7}$$

where *m* is the number of experimental data.

The McAllister model parameters which we have obtained for correlating experimental kinematic viscosity for each of the binary mixtures at the studied temperatures and the parameters estimated by means of the Asfour method are gathered together with MRSD in Table 2. The overall MRSD average is 3.45% which is comparable to results obtained for other mixtures using this method [2,24]. The better agreement between experimental and estimated values have been obtained for 1,4-dioxane + 1-chlorohexane and 1,3-dioxolane + 1-chlorohexane mixtures while the greatest differences have been found for systems containing tetrahydrofuran and tetrahydropyran. In general, there are slight differences for each system in function of temperature.

Acknowledgements

We are grateful at Diputación General de Aragón, and Universidad de Zaragoza for financial support. I. Bandrés and I. Giner thank the predoctoral fellowship from D.G.A.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.11.009.

References

[1] B. Giner, I. Gascón, A. Villares, P. Cea, C. Lafuente, J. Chem. Eng. Data 51 (2006) 1321–1325.
[2] B. Giner, H. Artigas, M. Haro, C. Lafuente, M.C. López, J. Mol. Liq. 129 (2006) 176–180.
[3] B. Giner, I. Gascón, H. Artigas, M.C. López, C. Lafuente, Int. J. Thermophys. 27 (2006) 1406–1418.
[4] B. Giner, I. Bandrés, G. Pera, I. Giner, F.M. Royo, Phys. Chem. Liq. 45 (2007) 503–513.
[5] B. Giner, I. Gascón, H. Artigas, C. Lafuente, A. Galindo, J. Phys. Chem. B 111 (2007) 9588–9597.
[6] I. Giner, A. Villares, M. Haro, I. Gascón, C. Lafuente, J. Therm. Anal. Calorim. 90 (2007) 587–595.
[7] I. Bandrés, B. Giner, A. Villares, H. Artigas, C. Lafuente, J. Mol. Liq. 139 (2008) 138–142.
[8] R.A. McAllister, AIChE J. 6 (1960) 427–431.
[9] S.L. Oswal, P. Oswal, R.P. Phalak, Int. J. Thermophys. 17 (1996) 1255–1267.
[10] A.A. Asfour, E.F. Cooper, J. Wu, R.R. Zahran, Ind. Eng. Chem. Res. 30 (1991) 1666–1671.
[11] A.H. Nhaesi, A.A. Asfour, Ind. Eng. Chem. Res. 37 (1998) 4893–4897.
[12] D.T. Wu, Fluid Phase Equilibr. 30 (1986) 149–156.
[13] J.L. Chevalier, P. Petrino, Y. Gaston-Bonhomme, Chem. Eng. Sci. 43 (1988) 1303–1309.
[14] TRC Tables, Thermodynamic Tables-Non-Hydrocarbons, Selected Values of Properties of Chemical Compounds, Thermodynamic Research Center, Texas A&M University College Station, 1974.
[15] A. Inglese, J.P.E. Grolier, E. Wilhelm, Fluid Phase Equilibr. 15 (1984) 287–294.
[16] P. Brocos, E. Calvo, A. Amigo, R. Bravo, M. Pintos, A.H. Roux, G. Roux-Desgranges, J. Chem. Eng. Data 43 (1998) 112–116.
[17] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents: Physical Properties and Methods of Purification. Techniques of Chemistry, 4th ed., Wiley Interscience, New York, 1986.
[18] H.I. Paul, J. Krug, B. Gutsche, H. Knapp, J. Chem. Eng. Data 33 (1988) 453–460.
[19] C. Carvajal, K.S. Tolle, J. Smid, M. Szwarc, J. Am. Chem. Soc. 87 (1965) 5548.
[20] M.N. Roy, B. Sinha, V.K. Dakua, J. Chem. Eng. Data 51 (2006) 590–594.
[21] J. Timmermans, Physico-Chemical Constants of Pure Organic Compounds, vol. II, Elsevier, Amsterdam, 1965.
[22] M.F. Bolotnikov, Y.A. Neruchev, J. Chem. Eng. Data 48 (2003) 739–741.
[23] W.A. Al Gherwi, A.H. Nhaesi, A.A. Asfour, J. Solution Chem. 35 (2006) 455–470.
[24] A. Villares, S. Rodríguez, C. Lafuente, F.M. Royo, M.C. López, J. Solution Chem. 33 (2004) 1119–1133.