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Surface Tension of Mixtures of Tetrahydrofuran or Tetrahydropyran with Isomeric Chlorobutanes

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Experimental surface tensions for mixtures containing tetrahydrofuran or tetrahydropyran and 1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane, or 2-chloro-2-methylpropane, measured with a drop volume tensiometer, are reported at temperatures of 298.15 and 313.15 K. Taking into account the Li-model for the surface tension, the variation of the interaction energy parameters with surface area is estimated.

KEY WORDS: chlorobutane; Li-model; surface tension; tetrahydrofuran; tetrahydropyran.

1. INTRODUCTION

As part of our research on the thermophysical properties of liquid mixtures involving cyclic ethers and chloroalkanes [1–5], we have previously reported a surface tension study of mixtures containing 1,3-dioxolane or 1,4-dioxane with isomeric chlorobutanes [6]. Now, this paper presents experimental results of surface tensions for binary mixtures, tetrahydrofuran, or tetrahydropyran with isomeric chlorobutanes: 1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane, or 2-chloro-2-methylpropane at temperatures of 298.15 and 313.15 K. A search of the literature reveals no references for the surface tension of these systems.

Using our results for surface tension and vapor–liquid equilibrium [7] and taking into account the Li-model [8] for the surface tension, we have

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estimated, for the mixtures studied here, the variation of the interaction energy parameters between the mixture components with the surface area.

2. EXPERIMENTAL

The liquids used were tetrahydrofuran (purity better than 99.5%) and 1-chlorobutane, 2-chlorobutane, and 2-methyl-2-chloropropane (purity better than 99%) provided by Aldrich, 2-methyl-1-chloropropane (purity better than 99%) obtained from Fluka, and tetrahydropyran (purity better than 99%) obtained from Acros. The purities of these compounds were checked by both GC and comparing their measured density values with literature data. Comparisons between measured densities and literature values [9, 10] at 298.15 K are given in Table I. No further purification was considered necessary.

The surface tensions, σ, of the pure liquids and their mixtures were determined using a drop volume tensiometer, Lauda TVT-2. This tensiometer measures the volume of a drop detaching from a capillary of known diameter; detailed instrument design and experimental procedures have been described elsewhere [11]. The temperature was kept constant within ±0.01 K by means of an external Lauda E-200 thermostat. Densities needed to calculate surface tensions from volume drop determinations were measured using an Anton Paar DMA-58 vibrating tube densimeter. Details of the experimental procedures can be found in a previous paper [12]. The uncertainty of the surface tension measurements is ±0.5% and the corresponding reproducibility is better than $\pm 0.01\,\mathrm{mN \cdot m^{-1}}$. The surface tensions of the pure compounds at 298.15 and 313.15 K, along with literature values [13, 14] at 298.15 K, are shown in Table I.

Table I. Experimental Surface Tensions, σ, and Densities, ρ, of the Pure Compounds and Comparisons with Literature Data

Compound	$\rho (\mathrm{g \cdot cm^{-3}})$		$\sigma\ (\mathrm{mN \cdot m^{-1}})$		
	$T = 298.15\,\mathrm{K}$		$T = 298.15\,\mathrm{K}$		$T = 313.15\,\mathrm{K}$
	Exptl.it		Exptl.it		
Tetrahydrofuran	0.88195	0.88197 [9]	27.04	27.04 [13]	25.05
Tetrahydropyran	0.87881	0.87916 [10]	27.29		25.39
1-Chlorobutane	0.88069	0.88095 [9]	23.29	23.1 [14]	21.58
2-Chlorobutane	0.86737	0.8671 [9]	21.83		19.33
1-Chloro-2-methylpropane	0.87113	0.8719 [9]	21.80	21.4 [14]	19.18
2-Chloro-2-methylpropane	0.83645	0.8361 [9]	18.90		16.98

Table II. Experimental Surface Tensions, σ, of the Binary Mixtures

x_1	σ $(\mathrm{mN \cdot m^{-1}})$	x_1	σ $(\mathrm{mN \cdot m^{-1}})$	x_1	σ $(\mathrm{mN \cdot m^{-1}})$
Tetrahydrofuran (1) + 1-chlorobutane (2) at 298.15 K					
0.0526	23.45	0.4671	24.65	0.8400	26.16
0.1121	23.62	0.5624	25.00	0.9224	26.58
0.2436	23.98	0.6678	25.41	0.9739	26.87
0.3549	24.29	0.7575	25.79		
Tetrahydrofuran (1) + 2-chlorobutane (2) at 298.15 K					
0.0427	21.96	0.4628	23.68	0.8400	25.77
0.1259	22.24	0.5654	24.19	0.9208	26.35
0.2478	22.71	0.6678	24.74	0.9701	26.76
0.3589	23.19	0.7513	25.22		
Tetrahydrofuran (1) + 1-chloro-2-methylpropane (2) at 298.15 K					
0.0652	22.25	0.4622	23.94	0.8408	25.89
0.1201	22.54	0.5682	24.44	0.9257	26.45
0.2392	23.06	0.6614	24.90	0.9662	26.75
0.3613	23.53	0.7586	25.42		
Tetrahydrofuran (1) + 2-chloro-2-methylpropane (2) at 298.15 K					
0.0664	19.32	0.4851	22.11	0.8446	25.20
0.1332	19.74	0.5768	22.81	0.9372	26.23
0.2532	20.51	0.6804	23.66	0.9656	26.58
0.3652	21.26	0.7747	24.51		
Tetrahydrofuran (1) + 1-chlorobutane (2) at 313.15 K					
0.0654	21.78	0.4658	22.89	0.8401	24.30
0.1272	21.95	0.5586	23.20	0.9272	24.69
0.2500	22.28	0.6569	23.56	0.9663	24.88
0.3654	22.59	0.7489	23.92		
Tetrahydrofuran (1) + 2-chlorobutane (2) at 313.15 K					
0.0581	19.70	0.4761	22.05	0.8360	23.94
0.1240	20.12	0.5730	22.53	0.9209	24.49
0.2442	20.84	0.6654	23.00	0.9663	24.81
0.3595	21.47	0.7524	23.45		
Tetrahydrofuran (1) + 1-chloro-2-methylpropane (2) at 313.15 K					
0.0619	19.77	0.4722	22.06	0.8338	23.88
0.1268	20.25	0.5669	22.51	0.9198	24.42
0.2531	21.00	0.6590	22.97	0.9751	24.83
0.3590	21.53	0.7539	23.45		
Tetrahydrofuran (1) + 2-chloro-2-methylpropane (2) at 313.15 K					
0.0427	16.98	0.3852	18.94	0.7940	22.48
0.1236	17.22	0.5033	19.90	0.8900	23.53
0.1853	17.54	0.6055	20.75	0.9446	24.25
0.2856	18.22	0.6963	21.55		

Table II. Continued

x_1	σ (mN · m^{-1})	x_1	σ (mN · m^{-1})	x_1	σ (mN · m^{-1})
Tetrahydropyran (1) + 1-chlorobutane (2) at 298.15 K					
0.0421	23.43	0.4245	24.82	0.8105	26.43
0.1082	23.65	0.5222	25.21	0.9103	26.88
0.2121	24.02	0.6243	25.63	0.9655	27.13
0.3174	24.41	0.7209	26.04		
Tetrahydropyran (1) + 2-chlorobutane (2) at 298.15 K					
0.0400	22.05	0.4166	23.88	0.8098	26.15
0.1057	22.38	0.5188	24.44	0.9438	26.95
0.2133	22.88	0.6151	24.99	0.9845	27.20
0.3195	23.39	0.7111	25.56		
Tetrahydropyran (1) + 1-chloro-2-methylpropane (2) at 298.15 K					
0.0483	22.18	0.4148	24.07	0.8079	26.15
0.1067	22.55	0.5190	24.58	0.9077	26.72
0.2075	23.09	0.6219	25.11	0.9602	27.04
0.3200	23.63	0.7194	25.65		
Tetrahydropyran (1) + 2-chloro-2-methylpropane (2) at 298.15 K					
0.0332	19.18	0.4336	22.17	0.8149	25.41
0.0955	19.68	0.5374	22.97	0.9089	26.36
0.2242	20.68	0.6269	23.69	0.9418	26.71
0.3219	21.37	0.7173	24.48		
Tetrahydropyran (1) + 1-chlorobutane (2) at 313.15 K					
0.0319	21.69	0.4209	23.04	0.8126	24.59
0.1092	21.95	0.5149	23.39	0.9067	24.99
0.2080	22.29	0.6199	23.80	0.9650	25.24
0.3137	22.66	0.7170	24.19		
Tetrahydropyran (1) + 2-chlorobutane (2) at 313.15 K					
0.0355	19.56	0.4243	22.14	0.8156	24.31
0.1006	20.01	0.5166	22.66	0.9057	24.85
0.2177	20.83	0.5931	23.07	0.9910	25.34
0.3192	21.50	0.7193	23.76		
Tetrahydropyran (1) + 1-chloro-2-methylpropane (2) at 313.15 K					
0.0377	19.55	0.4213	22.13	0.8148	24.37
0.1032	20.11	0.5302	22.74	0.9051	24.89
0.2167	20.92	0.6241	23.27	0.9660	25.22
0.3226	21.57	0.7134	23.78		
Tetrahydropyran (1) + 2-chloro-2-methylpropane (2) at 313.15 K					
0.0734	17.35	0.4363	19.80	0.8154	23.08
0.1038	17.50	0.5116	20.41	0.9006	23.98
0.2093	18.14	0.6120	21.24	0.9529	24.66
0.3169	18.90	0.7058	22.05		

The mixtures were prepared by weighing using a Sartorius CP225D balance. The maximum estimated uncertainty in the mole fraction is $\pm 1 \times 10^{-4}$.

3. RESULTS AND DISCUSSION

The surface tensions of the studied binary mixtures at temperatures of 298.15 and 313.15 K are given in Table II, and they are graphically represented in Figs. 1–4.

The surface tensions were correlated by means of a Redlich–Kister equation [15] of the form,

$$\sigma = x_1\sigma_1 + x_2\sigma_2 + x_1x_2\sum_{p=0}^{r} A_p(x_1 - x_2)^p \tag{1}$$

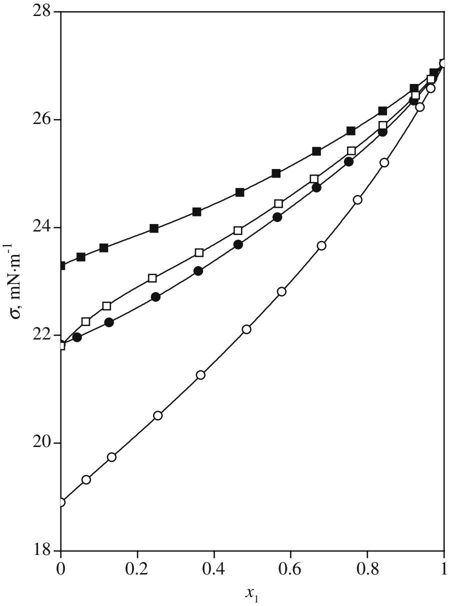

Fig. 1. Surface tensions, σ, at 298.15 K for tetrahydrofuran (1) with isomeric chlorobutanes (2): (■) 1-chlorobutane; (●) 2-chlorobutane; (○) 2-methyl-1-chloropropane; (□) 2-methyl-2-chloropropane; (—) Redlich–Kister equation.

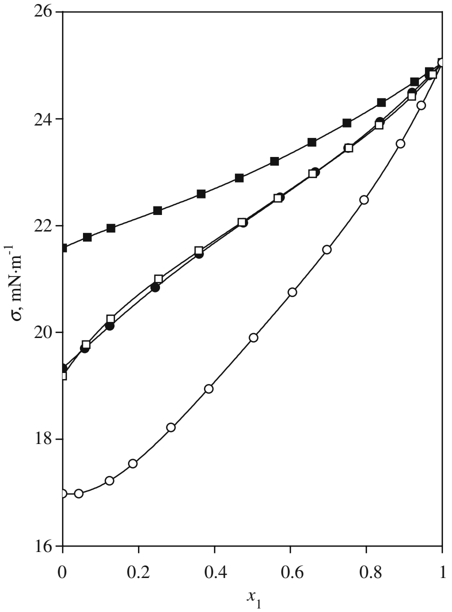

Fig. 2. Surface tensions, σ, at 313.15 K for tetrahydrofuran (1) with isomeric chlorobutanes (2): (■) 1-chlorobutane; (●) 2-chlorobutane; (□) 2-methyl-1-chloropropane; (○) 2-methyl-2-chloropropane; (—) Redlich–Kister equation.

where σ is the surface tension of the mixture; x_i and σ_i are the mole fraction and surface tension of component i, respectively; and A_p's are adjustable parameters determined by the method of least squares. The values of these parameters are given in Table III together with the corresponding average absolute deviations, AAD, between experimental and correlated values of the surface tension. The AAD is calculated by means of the expression,

$$\mathrm{AAD} = \frac{1}{N} \times \sum_{i=1}^{N} \left| \sigma_{i,\mathrm{exptl}} - \sigma_{i,\mathrm{cal}} \right|_i \tag{2}$$

where N is the number of experimental data.

The surface tension results for liquid mixtures are sometimes discussed in terms of surface tension deviations, $\Delta\sigma$, that is, the difference between the surface tension of the mixture and the surface tension calculated from a mole fraction average of the surface tension of the

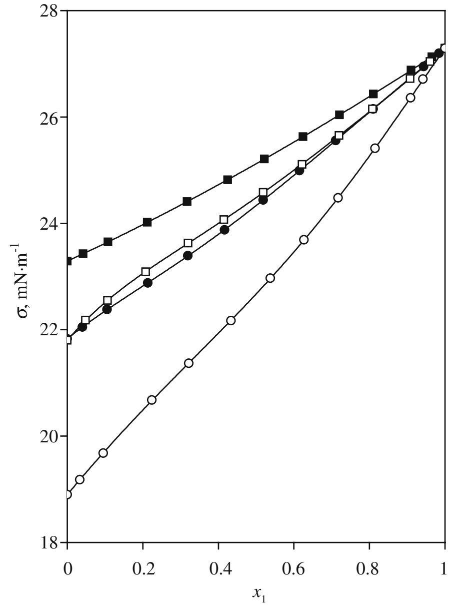

Fig. 3. Surface tensions, σ, at 298.15 K for tetrahydropyran (1) with isomeric chlorobutanes (2): (■) 1-chlorobutane; (●) 2-chlorobutane; (□) 2-methyl-1-chloropropane; (○) 2-methyl-2-chloropropane; (—) Redlich–Kister equation.

pure components [16–18]. Here, the most negative $\Delta\sigma$ values are reached for the mixtures containing the component with the lowest surface tension, that is, 2-chloro-2-methylpropane, and the most positive $\Delta\sigma$ values are reported for the mixtures containing 1-chloro-2-methylpropane. Taking into account the cyclic ethers, the $\Delta\sigma$ values for the mixtures containing tetrahydropyran are less negative than those with tetrahydrofuran.

The isomeric chlorobutanes are more surface active than the cyclic ethers and therefore are expected to be displaced to the surface, so $\Delta\sigma$ values should be negative [19]. However, the existence of specific interactions between the mixture components can lead to less negative or even positive $\Delta\sigma$ values when the difference among the surface tensions of the pure components is not too large; in these mixtures the existence of specific interactions is supported by their negative excess Gibbs functions values [7].

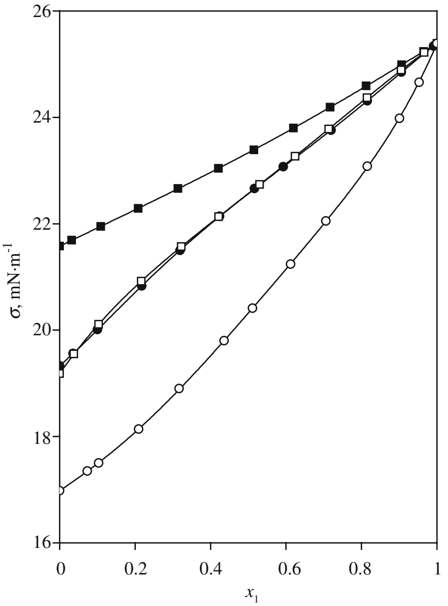

Fig. 4. Surface tensions, σ, at 313.15 K for tetrahydropyran (1) with isomeric chlorobutanes (2): (■) 1-chlorobutane; (●) 2-chlorobutane; (□) 2-methyl-1-chloropropane; (○) 2-methyl-2-chloropropane; (—) Redlich–Kister equation.

4. LI-MODEL CORRELATION

Li et al. [8] proposed a surface tension equation based on the thermodynamic definition of surface tension and the Wilson equation [20]. The expression for the surface tension of a liquid mixture is

$$\sigma = \sum x_i \sigma_i - RT \sum_i \frac{x_i}{\sum_j x_j \Lambda_{ij}} \sum_j x_j \left(\frac{\partial \Lambda_{ij}}{\partial A} \right)_{P,T,x} \tag{3}$$

where

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \tag{4}$$

and

$$\left(\frac{\partial \Lambda_{ij}}{\partial A} \right)_{P,T,x} = -\frac{\Lambda_{ij}}{RT} \left(\frac{\partial \left(\lambda_{ij} - \lambda_{ii} \right)}{\partial A} \right)_{P,T,x} \tag{5}$$

Table III. Parameters of the Redlich–Kister Equation and Average Absolute Deviations

System	T (K)	A_0	A_1	A_2	A_3	AAD ($\mathrm{mN \cdot m^{-1}}$)
Tetrahydrofuran+						
1-Chlorobutane	298.15	−1.57	−0.40	0.03	−0.77	0.00
	313.15	−1.24	−0.37	0.35	−0.38	0.00
2-Chlorobutane	298.15	−2.28	−0.44	−0.98	−0.68	0.00
	313.15	−0.07	−1.67	−0.43	0.49	0.00
1-Chloro-2-methylpropane	298.15	−1.21	−1.39	0.80	−1.79	0.00
	313.15	0.33	−2.18	0.57	−1.75	0.00
2-Chloro-2-methylpropane	298.15	−2.98	−1.35	−0.62	−0.57	0.00
	313.15	−4.55	0.15	−3.58	0.60	0.01
Tetrahydropyran+						
1-Chlorobutane	298.15	−0.68	0.03	−0.02	0.04	0.00
	313.15	−0.60	−0.08	0.18	0.06	0.00
2-Chlorobutane	298.15	−0.91	0.20	0.72	−0.64	0.00
	313.15	0.82	−1.10	−0.45	1.29	0.00
1-Chloro-2-methylpropane	298.15	−0.24	−0.97	1.26	−0.93	0.00
	313.15	1.13	−1.27	1.46	−0.10	0.00
2-Chloro-2-methylpropane	298.15	−1.69	−1.60	0.94	0.76	0.00
	313.15	−3.46	−0.50	−2.38	−1.75	0.01

where x_i, σ_i, and v_i are the mole fraction, surface tension, and molar volume of component i, respectively, R is the universal gas constant, T is the temperature, A is the surface area, and λ_{ij} is the interaction energy between components i and j.

For correlation of the surface tension of binary mixtures, there are four adjustable parameters. If one assumes that the energy parameters, $\lambda_{12}-\lambda_{11}$ and $\lambda_{22}-\lambda_{22}$, are the same as those obtained in the correlation of isothermal vapor–liquid equilibrium results, then only two parameters $(\partial(\lambda_{12}-\lambda_{11})/\partial A)_{P,T,x}$ and $(\partial(\lambda_{21}-\lambda_{22})/\partial A)_{P,T,x}$ need to be determined.

We have used the Wilson parameters obtained in the correlation of excess Gibbs functions of the mixtures of tetrahydrofuran or tetrahydropyran with isomeric chlorobutanes [7]; these parameters are given in Table IV. Estimation of the specific parameters of the Li model was based on minimization using the Marquardt algorithm [21] of the following objective function:

$$F=\sum_{i=1}^{n}\left(\sigma_{\mathrm{exptl}}-\sigma_{\mathrm{Li}}\right)_i^2 \tag{6}$$

Table IV. Wilson VLE-Parameters and Adjustable Parameters for Li Model along with Corresponding Average Absolute Deviations

System	T (K)	$\lambda_{12}-\lambda_{11}$ ($\text{J}\cdot\text{mol}^{-1}$)	$\lambda_{21}-\lambda_{22}$ ($\text{J}\cdot\text{mol}^{-1}$)	$\frac{\partial(\lambda_{12}-\lambda_{11})}{\partial A}$ ($\text{mJ}\cdot\text{mol}^{-1}\cdot\text{m}^{-2}$)	$\frac{\partial(\lambda_{21}-\lambda_{22})}{\partial A}$ ($\text{mJ}\cdot\text{mol}^{-1}\cdot\text{m}^{-2}$)	AAD ($\text{mN}\cdot\text{m}^{-1}$)
Tetrahydrofuran+						
1-Chlorobutane	298.15	721.52	−1013.98	−13.9	11.2	0.01
	313.15	−524.45	400.26	−7.5	10.0	0.01
2-Chlorobutane	298.15	628.71	−836.08	−18.5	15.7	0.03
	313.15	713.13	−930.29	−35.8	34.0	0.01
1-Chloro-2-methylpropane	298.15	2018.67	−2018.67	−12798.9	7370.1	0.04
	313.15	1720.23	−1821.30	−177.7	117.8	0.02
2-Chloro-2-methylpropane	298.15	−734.92	1303.28	2.3	−9.8	0.00
	313.15	−327.59	551.29	−26.8	36.5	0.11
Tetrahydropyran+						
1-Chlorobutane	298.15	−1143.45	1143.45	1978.6	−3366.2	0.01
	313.15	1151.61	1151.59	−1193.7	1995.3	0.01
2-chlorobutane	298.15	−895.13	895.13	−994.8	1553.1	0.02
	313.15	−816.39	816.38	2670.6	−3990.1	0.02
1-Chloro-2-methylpropane	298.15	−1162.21	1162.21	28816.9	−49941.5	0.05
	313.15	−1089.41	1089.42	4208.9	−6953.5	0.00
2-Chloro-2-methylpropane	298.15	3011.75	−2018.69	−18.3	−8.2	0.03
	313.15	915.06	−797.77	68.4	−59.2	0.08

These parameters are given for each mixture in Table IV together with the corresponding average absolute deviations AAD, between correlated and experimental values of the surface tension. Results show that the Li model correlates satisfactorily the experimental σ values, with an overall AAD equal to $0.35\,\mathrm{mN \cdot m^{-1}}$; the largest deviations are observed for the mixture of tetrahydropyran with 2-methyl-2-chloropropane at 313.15 K.

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