Study of the Surface Tension of Chlorocyclohexane or Bromocyclohexane with Some Cyclic Ethers

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Experimental surface tensions for mixtures formed by chlorocyclohexane or bromocyclohexane and a cyclic ether (tetrahydropyran, tetrahydrofuran, 2-methyltetrahydrofuran, or 2,5-dimethyltetrahydrofuran) have been measured with a drop volume tensiometer at temperatures of 298.15 K and 313.15 K. The surface tension deviations for the binary mixtures, that is, for each mixture, the deviation of the surface tension from a mole fraction average, have been calculated from the experimental data.

Introduction

Surface tension can be considered to be the result of several phenomena that take place not only in the surface but also in the bulk region of the liquid. An understanding of the structure and specific molecular interactions of the pure compounds and their mixtures can be obtained from surface tension data. Bulk thermodynamic properties such as excess volume or excess molar enthalpies can provide similar information,[1−3] but by using the surface tension, we try to obtain a broader vision. Besides, in chemical engineering, surface tension not only determines the quality of many industrial products but also affects some important steps in production process of catalysis or adsorption.

In a previous paper,[4] we reported the surface tensions of mixtures containing cyclohexane and methylcyclohexane with tetrahydropyran, tetrahydrofuran, 2-methyltetrahydrofuran, or 2,5-dimethyltetrahydrofuran. In the present paper, we report the surface tensions of mixtures containing chlorocyclohexane or bromocyclohexane with the same cyclic ethers at 298.15 K and 313.15 K; from these data surface tension deviations have been obtained.

A revision of the literature shows that there are not references for the surface tensions of these systems.

Experimental Section

Chemicals. The liquids used in the experimental measurements were obtained from Aldrich and had the following mass purities: chlorocyclohexane and 2-methyltetrahydrofuran, >99%; tetrahydrofuran, >99.5%. Tetrahydropyran and 2,5-dimethyl-tetrahydrofuran (>99%) were provided by Acros, and bromocyclohexane (>99%) was obtained from Fluka. All of the substances were used without further purification.

Apparatus and Procedures. The surface tensions, σ, of the pure liquids and their mixtures were determined using a Lauda TVT-2 drop volume tensiometer.[6] The temperature was kept constant to within ±0.01 K by means of an external Lauda E-200 thermostat. Densities needed to calculate surface tensions from volume drop determinations and densities of pure compounds were measured using an Anton Paar DMA-58 vibrating tube densimeter.

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Table 1. Experimental and Literature Data of Densities, ρ, and Surface Tensions, σ, of Pure Components at 298.15 K

	ρ/g·cm^{-3}		σ/mN·m^{-1}	
compound	exptl	lit	exptl	lit
chlorocyclohexane	0.99317		31.05	
bromocyclohexane	1.32841		33.63	
tetrahydropyran	0.87882	0.87916[a]	27.29	
tetrahydrofuran	0.88210	0.88197[b]	27.12	27.04[d]
2-methyltetrahydrofuran	0.84940	0.84882[c]	24.56	
2,5-dimethyltetrahydrofuran	0.82525		22.93	

[a] Reference 8. [b] Reference 9. [c] Reference 10. [d] Reference 11.

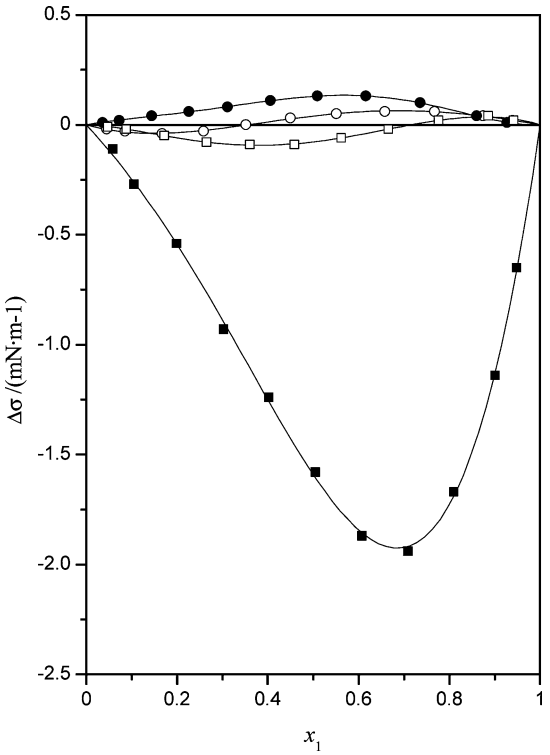

Figure 1. Surface tension deviations, $\Delta\sigma$, of chlorocyclohexane with (○) tetrahydropyran, (●) tetrahydrofuran, (□) 2-methyltetrahydrofuran, or (■) 2,5-dimethyltetrahydrofuran at 298.15 K.

Details of the experimental procedure can be found in a previous paper.[7] The uncertainty of the surface tension

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Table 2. Experimental Surface Tensions, σ, and Surface Tension Deviations, $\Delta\sigma$, of the Mixtures Studied

x_1	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}	x_1	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}	x_1	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}	x_1	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}
Chlorocyclohexane (1) + Tetrahydropyran (2) at 298.15 K											
0.0000	27.29	0.00	0.2584	28.23	−0.03	0.5511	29.41	0.05	0.8744	30.62	0.04
0.0446	27.44	−0.02	0.3519	28.62	0.00	0.6580	29.82	0.06	0.9393	30.84	0.02
0.0850	27.58	−0.03	0.4501	29.01	0.03	0.7676	30.24	0.06	1.0000	31.05	0.00
0.1673	27.88	−0.04									
Chlorocyclohexane (1) + Tetrahydrofuran (2) at 298.15 K											
0.0000	27.12	0.00	0.2258	28.07	0.06	0.5093	29.25	0.13	0.8602	30.54	0.04
0.0362	27.27	0.01	0.3114	28.43	0.08	0.6163	29.68	0.13	0.9267	30.77	0.01
0.0728	27.43	0.02	0.4061	28.82	0.11	0.7359	30.11	0.10	1.0000	31.05	0.00
0.1442	27.73	0.04									
Chlorocyclohexane (1) + 2-Methyltetrahydrofuran (2) at 298.15 K											
0.0000	24.56	0.00	0.2652	26.20	−0.08	0.5615	28.15	−0.06	0.8856	30.34	0.04
0.0471	24.85	−0.01	0.3605	26.81	−0.09	0.6654	28.86	−0.02	0.9418	30.70	0.02
0.0884	25.11	−0.02	0.4587	27.44	−0.09	0.7761	29.62	0.02	1.0000	31.05	0.00
0.1722	25.63	−0.05									
Chlorocyclohexane (1) + 2,5-Dimethyltetrahydrofuran (2) at 298.15 K											
0.0000	22.93	0.00	0.3031	24.46	−0.93	0.6071	25.99	−1.87	0.9009	29.10	−1.14
0.0582	23.29	−0.11	0.4025	24.96	−1.24	0.7088	26.75	−1.94	0.9482	29.98	−0.65
0.1048	23.51	−0.27	0.5047	25.45	−1.58	0.8097	27.83	−1.67	1.0000	31.05	0.00
0.1988	24.00	−0.54									
Chlorocyclohexane (1) + Tetrahydropyran (2) at 313.15 K											
0.0000	25.46	0.00	0.2590	26.55	0.06	0.5923	27.91	0.09	0.8809	29.02	0.05
0.0440	25.64	0.01	0.3527	26.94	0.07	0.6578	28.17	0.09	0.9385	29.22	0.03
0.0854	25.82	0.02	0.4499	27.33	0.08	0.7693	28.60	0.08	1.0000	29.44	0.00
0.1668	26.17	0.04									
Chlorocyclohexane (1) + Tetrahydrofuran (2) at 313.15 K											
0.0000	25.24	0.00	0.2257	26.25	0.07	0.5071	27.52	0.15	0.8582	28.89	0.05
0.0361	25.39	0.00	0.3114	26.66	0.11	0.6173	27.96	0.13	0.9291	29.16	0.02
0.0727	25.56	0.01	0.4061	27.09	0.14	0.7351	28.42	0.09	1.0000	29.44	0.00
0.1434	25.88	0.03									
Chlorocyclohexane (1) + 2-Methyltetrahydrofuran (2) at 313.15 K											
0.0000	23.02	0.00	0.2653	24.47	−0.25	0.5618	26.31	−0.32	0.8805	28.58	−0.10
0.0434	23.23	−0.07	0.3536	25.00	−0.29	0.6677	27.03	−0.28	0.9404	29.00	−0.05
0.0868	23.44	−0.13	0.4591	25.65	−0.32	0.7734	27.78	−0.20	1.0000	29.44	0.00
0.1719	23.93	−0.19									
Chlorocyclohexane (1) + 2,5-Dimethyltetrahydrofuran (2) at 313.15 K											
0.0000	21.50	0.00	0.3037	23.30	−0.61	0.6055	24.87	−1.44	0.9065	27.94	−0.76
0.0540	21.87	−0.06	0.4049	23.78	−0.93	0.7039	25.58	−1.51	0.9479	28.54	−0.48
0.0998	22.15	−0.14	0.5090	24.29	−1.25	0.8075	26.61	−1.30	1.0000	29.44	0.00
0.2020	22.76	−0.35									
Bromocyclohexane (1) + Tetrahydropyran (2) at 298.15 K											
0.0000	27.29	0.00	0.2960	29.11	−0.06	0.6178	31.23	0.03	0.8816	32.95	0.07
0.0539	27.62	−0.01	0.3969	29.75	−0.06	0.7120	31.86	0.06	0.9568	33.39	0.03
0.0980	27.89	−0.02	0.4993	30.43	−0.03	0.8067	32.49	0.08	1.0000	33.63	0.00
0.1908	28.45	−0.05									
Bromocyclohexane (1) + Tetrahydrofuran (2) at 298.15 K											
0.0000	27.12	0.00	0.2954	29.06	0.02	0.6110	31.24	0.14	0.8937	32.98	0.05
0.0528	27.39	−0.07	0.3997	29.82	0.10	0.7127	31.89	0.13	0.9467	33.31	0.02
0.0909	27.62	−0.09	0.5057	30.56	0.14	0.8232	32.56	0.08	1.0000	33.63	0.00
0.1919	28.31	−0.06									
Bromocyclohexane (1) + 2-Methyltetrahydrofuran (2) at 298.15 K											
0.0000	24.56	0.00	0.2908	26.95	−0.24	0.5896	29.55	−0.36	0.9043	32.65	−0.11
0.0420	24.87	−0.07	0.3921	27.82	−0.29	0.6994	30.58	−0.33	0.9247	32.86	−0.09
0.0933	25.28	−0.13	0.5072	28.82	−0.34	0.8173	31.75	−0.22	1.0000	33.63	0.00
0.1942	26.13	−0.19									
Bromocyclohexane (1) + 2,5-Dimethyltetrahydrofuran (2) at 298.15 K											
0.0000	22.93	0.00	0.2942	24.54	−1.54	0.6382	26.39	−3.37	0.8996	31.47	−1.09
0.0692	23.30	−0.37	0.3981	24.90	−2.29	0.8032	29.16	−2.36	0.9378	32.34	−0.62
0.0908	23.42	−0.48	0.4712	25.17	−2.80	0.8552	30.35	−1.73	1.0000	33.63	0.00
0.1916	24.03	−0.95	0.5994	25.96	−3.38						
Bromocyclohexane (1) + Tetrahydropyran (2) at 313.15 K											
0.0000	25.46	0.00	0.2960	27.70	0.02	0.6178	29.74	−0.37	0.8816	31.88	−0.21
0.0539	25.95	0.09	0.3969	28.35	−0.10	0.7120	30.43	−0.39	0.9568	32.57	−0.09
0.0980	26.32	0.12	0.4993	28.98	−0.24	0.8067	31.23	−0.30	1.0000	32.98	0.00
0.1908	27.01	0.11									
Bromocyclohexane (1) + Tetrahydrofuran (2) at 313.15 K											
0.0000	25.24	0.00	0.2954	27.39	−0.13	0.6110	29.65	−0.32	0.8994	32.00	−0.20
0.0528	25.66	0.01	0.3997	28.12	−0.21	0.7127	30.42	−0.34	0.9467	32.44	−0.12
0.0909	25.94	0.00	0.5057	28.88	−0.28	0.8064	31.18	−0.30	1.0000	32.98	0.00
0.1919	26.67	−0.05									
Bromocyclohexane (1) + 2-Methyltetrahydrofuran (2) at 313.15 K											
0.0000	23.02	0.00	0.2908	25.48	−0.43	0.5896	28.19	−0.71	0.9043	31.55	−0.48
0.0420	23.36	−0.08	0.3921	26.38	−0.54	0.6994	29.24	−0.75	0.9247	31.85	−0.38
0.0933	23.78	−0.17	0.5072	27.43	−0.65	0.8173	30.49	−0.67	1.0000	32.98	0.00
0.1942	24.63	−0.32									
Bromocyclohexane (1) + 2,5-Dimethyltetrahydrofuran (2) at 313.15 K											
0.0000	21.50	0.00	0.2942	23.16	−1.72	0.6382	25.15	−3.68	0.8558	28.40	−2.92
0.0692	21.71	−0.58	0.3981	23.73	−2.34	0.7010	25.74	−3.81	0.9378	30.81	−1.46
0.0908	21.83	−0.71	0.4712	24.06	−2.85	0.8035	27.31	−3.41	1.0000	32.98	0.00
0.1916	22.52	−1.18	0.5994	24.84	−3.54						

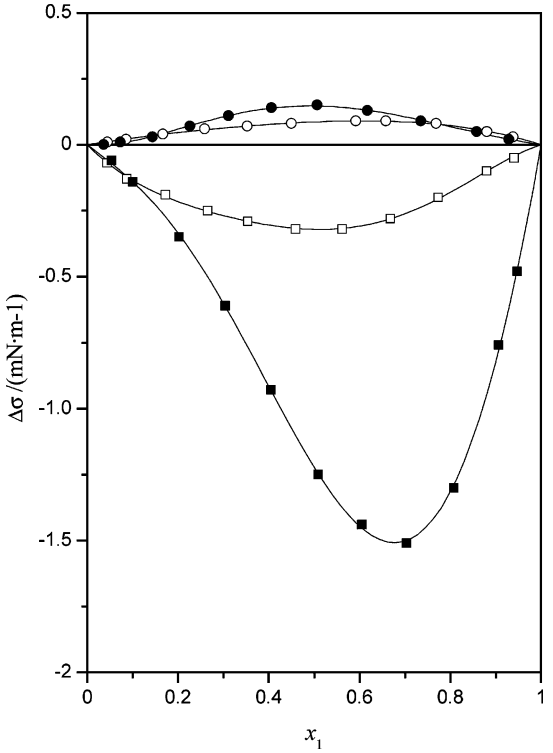

Figure 2. Surface tension deviations, $\Delta\sigma$, of chlorocyclohexane with (○) tetrahydropyran, (●) tetrahydrofuran, (□) 2-methyltetrahydrofuran, or (■) 2,5-dimethyltetrahydrofuran at 313.15 K.

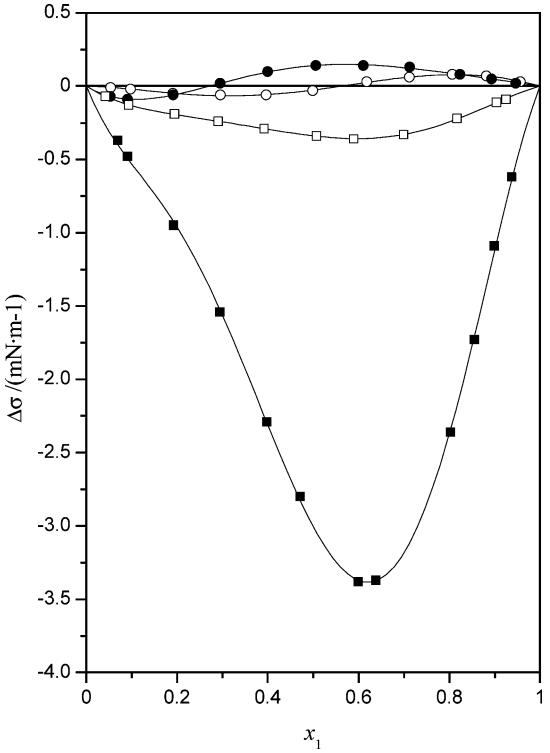

Figure 3. Surface tension deviations, $\Delta\sigma$, of bromocyclohexane with (○) tetrahydropyran, (●) tetrahydrofuran, (□) 2-methyltetrahydrofuran, or (■) 2,5-dimethyltetrahydrofuran at 298.15 K.

measurement is ±0.01 mN·m^{-1}. Surface tensions and densities of the pure compounds at 298.15 K, along with literature values,[8−11] are shown in Table 1.

The mixtures were prepared by mass using a Mettler H20T balance. The maximum estimated error in the mole fraction is $\pm 1 \times 10^{-4}$.

Results

The surface tensions of the studied binary mixtures are given in Table 2. Surface tension deviations, $\Delta\sigma$, were calculated from our measurements according to the following equation

$$\Delta\sigma/\mathrm{mN{\cdot}m^{-1}} = \sigma - x_1\sigma_1 - x_2\sigma_2 \qquad (1)$$

where σ is the surface tension of the mixture and x_i and σ_i are the mole fraction and surface tension of component i, respectively. The values of surface tension deviations are also given in Table 2, and they are graphically represented in Figures 1 to 4.

The surface tension deviations were correlated by means of the Redlich−Kister equation

$$\Delta\sigma/\mathrm{mN{\cdot}m^{-1}} = x_1x_2\sum_{p=0}^{r}A_p(x_1 - x_2)^p \qquad (2)$$

where A_p are adjustable parameters determined by the method of least squares without using any statistical weights. The values of these parameters at each temperature are given in Table 3 together with the standard deviations, $s(\Delta\sigma)$, calculated as follows

$$s(\Delta\sigma) = \left[\frac{\sum_{i=1}^{n}(\Delta\sigma_{\mathrm{calcd}} - \Delta\sigma_{\mathrm{exptl}})^2}{(n-p)}\right]^{1/2} \qquad (3)$$

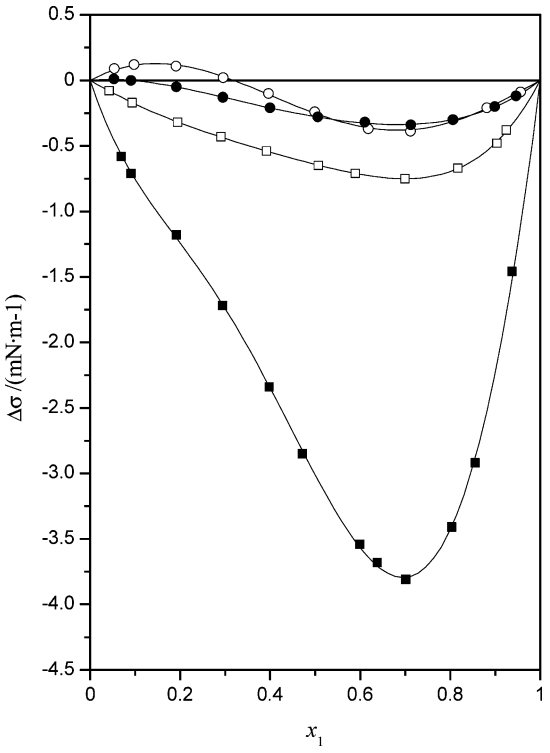

Figure 4. Surface tension deviations, $\Delta\sigma$, of bromocyclohexane with (○) tetrahydropyran, (●) tetrahydrofuran, (□) 2-methyltetrahydrofuran, or (■) 2,5-dimethyltetrahydrofuran at 313.15 K.

where n is the number of experimental data points and p is the number of parameters.

The surface behavior of the mixtures containing chlorocyclohexane and bromocyclohexane is similar. Taking into account the cyclic ethers, we find that the $\Delta\sigma$ values follow the sequence tetrahydrofuran > tetrahydropyran > 2-methyltetrahydrofuran > 2,5-dimethyltetrahydrofuran, al-

Table 3. Parameters, A_i, and Standard Deviations, $S(\Delta\sigma)$, for the Redlich−Kister Equation (Equation 2)

T/K	A_0	A_1	A_2	A_3	$s(\Delta\sigma)$
Chlorocyclohexane (1) + Tetrahydropyran (2)					
298.15	0.16	0.47	−0.28		0.003
313.15	0.35	0.14	0.07		0.002
Chlorocyclohexane (1) + Tetrahydrofuran (2)					
298.15	0.52	0.28	−0.38	−0.51	0.002
313.15	0.59	−0.04	−0.53	0.24	0.003
Chlorocyclohexane (1) + 2-Methyltetrahydrofuran (2)					
298.15	−0.31	0.50	0.58	−0.14	0.004
313.15	−1.28	−0.07	0.13	0.71	0.019
Chlorocyclohexane (1) + 2,5-Dimethyltetrahydrofuran (2)					
298.15	−6.36	−6.16	−2.06		0.023
313.15	−4.89	−5.57	−0.73	1.28	0.013
Bromocyclohexane (1) + Tetrahydropyran (2)					
298.15	−0.10	0.79	0.53	−0.32	0.004
313.15	−1.00	−2.50	1.00	0.65	0.012
Bromocyclohexane (1) + Tetrahydrofuran (2)					
298.15	0.56	0.50	−1.26	0.69	0.005
313.15	−1.11	−1.16	−0.04	−0.35	0.004
Bromocyclohexane (1) + 2-Methyltetrahydrofuran (2)					
298.15	−1.35	−0.72	−0.06	1.29	0.003
313.15	−2.57	−1.74	−1.73	−0.53	0.007
Bromocyclohexane (1) + 2,5-Dimethyltetrahydrofuran (2)					
298.15	−12.02	−11.50	4.45	11.56	0.026
313.15	−12.05	−12.86	−7.10	4.08	0.032

though at 313.15 K $\Delta\sigma$ values for the mixture containing bromocyclohexane and tetrahydrofuran are smaller than in the case of the mixture formed by bromocyclohexane and tetrahydropyran when the mole fraction of the ether is less than 0.5. We can remark that the $\Delta\sigma$ values for the mixtures containing 2,5-dimethyltetrahydrofuran are negative and much higher in absolute value than for the rest of the mixtures.

The cyclic ethers present lower surface tension values than chlorocyclohexane or bromocyclohexane. They are more surface-active and therefore are expected to be displaced to the surface (Gibbs adsorption) whereas the halocyclohexanes will tend to stay in the bulk. Therefore, the surface tension deviation values should be negative, and the higher difference between surface tension of pure components, the more negative the surface tension deviations should be. Nevertheless, if there are specific interactions between the mixed compounds and the difference between their surface tension values is not too high, then the surface tension deviation can be positive. Therefore, the positive $\Delta\sigma$ values presented by some of our mixtures can be explained by taking into account the existence of Cl−O[12] and Br−O specific interactions.

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