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Excess Volumes and Excess Viscosities of Binary Mixtures of Some Cyclic Ethers + Bromocyclohexane at 298.15 and 313.15 K

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Excess volumes, V^E, and excess viscosities, η^E, at 298.15 and 313.15 K are reported for binary mixtures of some cyclic ethers (tetrahydrofuran, tetrahydropyran, 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran) + bromocyclohexane. These properties were obtained from density and viscosity measurements. V^E and η^E show negatives values for all the mixtures.

KEY WORDS: binary mixtures; cyclic ethers; bromocyclohexane; excess volume; excess viscosity.

1. INTRODUCTION

A survey of the literature shows that studies of excess properties of binary mixtures containing tetrahydrofuran are abundant but they are scarce for other cyclic ethers such as tetrahydropyran and, especially 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran. With the aim of enlarge the experimental results on thermodynamic and transport properties of mixtures involving these compounds, we have begun a study of excess properties of binary mixtures containing a cyclic ether and a haloalkane. In this paper we present excess volumes and excess viscosities of binary mixtures of some cyclic ethers (tetrahydrofuran, tetrahydropyran, 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran) with bromocyclohexane at the temperatures 298.15 and 313.15 K.

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2. EXPERIMENTS

The liquids used were tetrahydrofuran (better than 99.5% purity), tetrahydropyran, 2-methyltetrahydrofuran, and 2,5-dimethyltetrahydrofuran (better than 99.0% purity) obtained from Aldrich and bromocyclohexane (better than 99.0% purity) provided by Fluka. The purity of chemicals was checked by GLC and was considered sufficient, so no further purification was attempted.

The densities of the pure components and mixtures were measured by means of an Anton-Paar DMA-58 vibrating tube densimeter automatically thermostated at ± 0.01 K. The accuracy of density measurements, after proper calibration, was $\pm 1 \times 10^{-5}\ g \cdot cm^{-3}$. The calibration was carried out with deionized doublydistilled water and dry air.

The viscosities were determined with an Ubbelhode viscosimeter and a Schott–Geräte automatic measuring unity model AVS-440. The temperature was kept constant within ± 0.01 K by means of Schott–Geräte thermostat. The accuracy of the time flow measurements was ± 0.01 s. The viscosimeter was calibrated with deionized doubly distilled water. Details of the procedure have been previously described [1]. 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 estimated error in the kinematic viscosity was $\pm 1 \times 10^{-4}\ mm^2 \cdot s^{-1}$.

The mixtures were prepared using a Mettler H20T balance. The possible error in the mole fractions is estimated to be less than ± 0.0001.

Table I shows the experimental values of density and viscosity for the pure compounds at 298.15 K in comparison with published values [2–6].

Table I. Densities, ρ, and Viscosities, η, of Pure Compounds at 298.15 K Compared with the Literature Data

	ρ ($g \cdot cm^{-3}$)		η (cP)	
Liquid	Expt.	Lit.	Expt.	Lit.
Tetrahydrofuran	0.88209	0.88197 [2]	0.4637	0.461 [3]
Tetrahydropyran	0.87915	0.87916 [4]	0.8008	0.764 [5]
2-Methyltetrahydrofuran	0.84990	0.84882 [6]	0.4835	0.4573 [6]
2,5-Dimethyltetrahydrofuran	0.82527	—	0.4850	—
Bromocyclohexane	1.32608	—	1.4052	—

3. RESULTS AND DISCUSSION

Excess volumes and excess viscosities were calculated from our measurements according to the following equations:

$$V^E = x_1 M_1(\rho^{-1} - \rho_1^{-1}) + x_2 M_2(\rho^{-1} - \rho_2^{-1}) \quad (1)$$

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \quad (2)$$

where M_i, ρ_i, η_i, and x_i designate the molar mass ($g \cdot mol^{-1}$), density ($g \cdot cm^{-3}$), viscosity (cP), and molar fraction of component i in the mixture. Subscript 1 is used for cyclic ethers; 2 for bromocyclohexane. Quantities without subscripts refer to the mixture.

The values of each property at each temperature were correlated with a Redlich–Kister polynomial equation:

$$Y^E = x_1(1 - x_1) \sum_{i=0}^{i=n} A_i(2x_1 - 1)^i \quad (3)$$

where $Y^E = V^E$ or η^E, A_i are adjustable parameters, and x_1 is the mole fraction of cyclic ether.

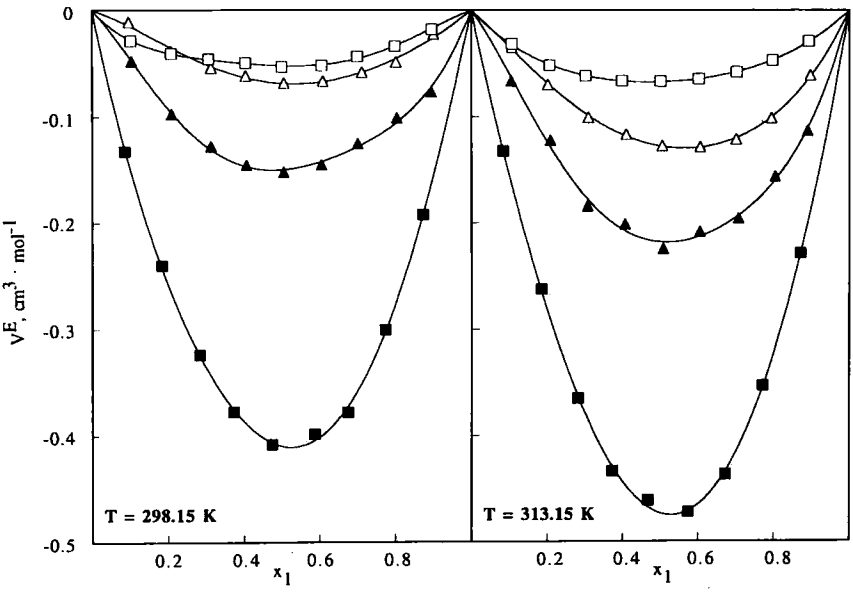

Fig. 1. Excess volumes, V^E, of cyclic ethers (1) + bromocyclohexane (2) at 298.15 and 313.15 K as a function of mole fraction x_1: tetrahydrofuran (△); tetrahydropyran (□); 2-methyl-tetrahydrofuran (▲); 2,5-dimethyl-tetrahydrofuran (■); (——) Redlich–Kister equations.

Table II. Excess Volumes, V^E, of Binary Mixtures of Cyclic Ethers (1) + Bromocyclohexane (2) at 298.15 and 313.15 K

T (K)	x_1	V^E ($cm^3 \cdot mol^{-1}$)	x_1	V^E ($cm^3 \cdot mol^{-1}$)	x_1	V^E ($cm^3 \cdot mol^{-1}$)
		Tetrahydrofuran (1) + bromocyclohexane (2)				
298.15	0.0954	−0.0111	0.4034	−0.0614	0.7111	−0.0583
	0.2064	−0.0382	0.5052	−0.0681	0.8009	−0.0486
	0.3118	−0.0538	0.6084	−0.0664	0.8999	−0.0224
		Tetrahydropyran (1) + bromocyclohexane (2)				
298.15	0.1010	−0.0287	0.4025	−0.0494	0.6990	−0.0434
	0.2077	−0.0406	0.4991	−0.0531	0.7978	−0.0336
	0.3055	−0.0457	0.6046	−0.0519	0.8951	−0.0179
		2-Methyltetrahydrofuran (1) + bromocyclohexane (2)				
298.15	0.1030	−0.0479	0.4055	−0.1454	0.7007	−0.1252
	0.2083	−0.0973	0.5045	−0.1520	0.8034	−0.1012
	0.3118	−0.1278	0.6049	−0.1450	0.8942	−0.0766
		2,5-Dimethyltetrahydrofuran (1) + bromocyclohexane (2)				
298.15	0.0849	−0.1323	0.3722	−0.3773	0.6749	−0.3780
	0.1827	−0.2397	0.4738	−0.4080	0.7729	−0.3005
	0.2826	−0.3238	0.5871	−0.3982	0.8729	−0.1922
		Tetrahydrofuran (1) + bromocyclohexane (2)				
313.15	0.1068	−0.0350	0.4093	−0.1167	0.7003	−0.1210
	0.2019	−0.0699	0.5049	−0.1273	0.7942	−0.1011
	0.3093	−0.1007	0.6051	−0.1283	0.8975	−0.0609
		Tetrahydropyran (1) + bromocyclohexane (2)				
313.15	0.1072	−0.0318	0.3985	−0.0664	0.7018	−0.0581
	0.2065	−0.0519	0.5007	−0.0667	0.7971	−0.0471
	0.3026	−0.0618	0.6020	−0.0646	0.8931	−0.0292
		2-Methyltetrahydrofuran (1) + bromocyclohexane (2)				
313.15	0.1057	−0.0667	0.4061	−0.2013	0.7063	−0.1960
	0.2082	−0.1223	0.5070	−0.2247	0.8037	−0.1561
	0.3069	−0.1844	0.6045	−0.2082	0.8901	−0.1133
		2,5-Dimethyltetrahydrofuran (1) + bromocyclohexane (2)				
313.15	0.0837	−0.1324	0.3729	−0.4335	0.6716	−0.4368
	0.1845	−0.2623	0.4670	−0.4610	0.7709	−0.3535
	0.2816	−0.3653	0.5738	−0.4724	0.8712	−0.2288

Table III. Excess Viscosities, η^E, of Binary Mixtures Cyclic Ethers (1) + Bromocyclohexane (2) at 298.15 and 313.15 K

T (K)	x_1	η^E (cP)	x_1	η^E (cP)	x_1	η^E (cP)
	Tetrahydrofuran (1) + bromocyclohexane (2)					
298.15	0.0951	−0.1049	0.4021	−0.2543	0.6981	−0.1940
	0.2028	−0.1882	0.5006	−0.2513	0.7997	−0.1517
	0.2992	−0.2343	0.6017	−0.2311	0.9044	−0.0730
	Tetrahydropyran (1) + bromocyclohexane (2)					
298.15	0.1315	−0.0673	0.3968	−0.1285	0.7001	−0.1007
	0.1990	−0.0921	0.5009	−0.1280	0.8009	−0.0742
	0.3035	−0.1188	0.6025	−0.1185	0.9018	−0.0397
	2-Methyltetrahydrofuran (1) + bromocyclohexane (2)					
298.15	0.1007	−0.1482	0.4047	−0.3098	0.7044	−0.2121
	0.2017	−0.2410	0.5012	−0.2898	0.7991	−0.1611
	0.3008	−0.2924	0.6038	−0.2584	0.9006	−0.0853
	2,5-Dimethyltetrahydrofuran (1) + bromocyclohexane (2)					
298.15	0.1016	−0.1656	0.3984	−0.3251	0.6987	−0.2369
	0.2001	−0.2615	0.5018	−0.3172	0.8104	−0.1603
	0.3052	−0.3188	0.6042	−0.2822	0.9017	−0.0878
	Tetrahydrofuran (1) + bromocyclohexane (2)					
313.15	0.0951	−0.0633	0.4021	−0.1634	0.6981	−0.1276
	0.2028	−0.1164	0.5006	−0.1620	0.7997	−0.0933
	0.2902	−0.1479	0.6017	−0.1507	0.9044	−0.0487
	Tetrahydropyran (1) + bromocyclohexane (2)					
313.15	0.1315	−0.0419	0.3968	−0.0829	0.7001	−0.0666
	0.1990	−0.0580	0.5009	−0.0818	0.8009	−0.0496
	0.3035	−0.0760	0.6025	−0.0785	0.9018	−0.0267
	2-Methyltetrahydrofuran (1) + bromocyclohexane (2)					
313.15	0.1007	−0.0954	0.4047	−0.2065	0.7044	−0.1430
	0.2017	−0.1576	0.5012	−0.2020	0.7991	−0.1106
	0.3008	−0.1924	0.6038	−0.1752	0.9006	−0.0586
	2,5-Dimethyltetrahydrofuran (1) + bromocyclohexane (2)					
313.15	0.1016	−0.1104	0.3984	−0.2289	0.6987	−0.1661
	0.2001	−0.1747	0.5018	−0.2199	0.8104	−0.1138
	0.3052	−0.2183	0.6042	−0.1973	0.9017	−0.0627

Table IV. Coefficients, A_i, in Eq. (3) and Standard Deviations, $\sigma(Y^E)$, Determined by the Least-Squares Method

	A_0	A_1	A_2	A_3	$\sigma(Y^E)$
Tetrahydrofuran + bromocyclohexane at 298.15 K					
V^E (cm^3 · mol^{-1})	−0.2743	−0.0423	0.0728	−0.0485	0.0031
η^E (cP)	−1.0087	0.2290	−0.0811	−0.0366	0.0037
Tetrahydropyran + bromocyclohexane at 298.15 K					
V^E (cm^3 · mol^{-1})	−0.2078	−0.0197	−0.0590	0.1565	0.0012
η^E (cP)	−0.5151	0.1033	−0.0165	−0.0215	0.0006
2-Methyltetrahydrofuran + bromocyclohexane at 298.15 K					
V^E (cm^3 · mol^{-1})	−0.5985	0.0507	−0.0621	−0.3356	0.0038
η^E (cP)	−1.1727	0.4804	−0.2065	−0.1185	0.0029
2,5-Dimethyltetrahydrofuran + bromocyclohexane at 298.15 K					
V^E (cm^3 · mol^{-1})	−1.6380	−0.1623	−0.0912	0.1919	0.0042
η^E (cP)	−1.2687	0.4528	−0.2185	0.1010	0.0026
Tetrahydrofuran + bromocyclohexane at 313.15 K					
V^E (cm^3 · mol^{-1})	−0.5107	−0.1219	−0.0305	−0.1010	0.0017
η^E (cP)	−0.6531	0.1296	−0.0021	−0.0368	0.0007
Tetrahydropyran + bromocyclohexane at 313.15 K					
V^E (cm^3 · mol^{-1})	−0.2695	0.0213	−0.0908	−0.0042	0.0006
η^E (cP)	−0.3342	0.0507	−0.0084	−0.0149	0.0010
2-Methyltetrahydrofuran + bromocyclohexane at 313.15 K					
V^E (cm^3 · mol^{-1})	−0.8721	−0.0545	−0.0520	−0.3919	0.0067
η^E (cP)	−0.7968	0.2946	−0.0864	−0.0946	0.0025
2,5-Dimethyltetrahydrofuran + bromocyclohexane at 313.15 K					
V^E (cm^3 · mol^{-1})	−1.8935	−0.2256	0.0064	0.0370	0.0040
η^E (cP)	−0.8861	0.3024	−0.1091	0.0008	0.0018

These properties for the mixtures are presented in Tables II and III, and they are shown graphically in Figs. 1 and 2. Table IV lists the values of the parameters A_i together with the standard deviations $\sigma(Y^E)$.

The excess volumes are negative over the entire composition range and increase in absolute value with increasing temperature. V^E increases

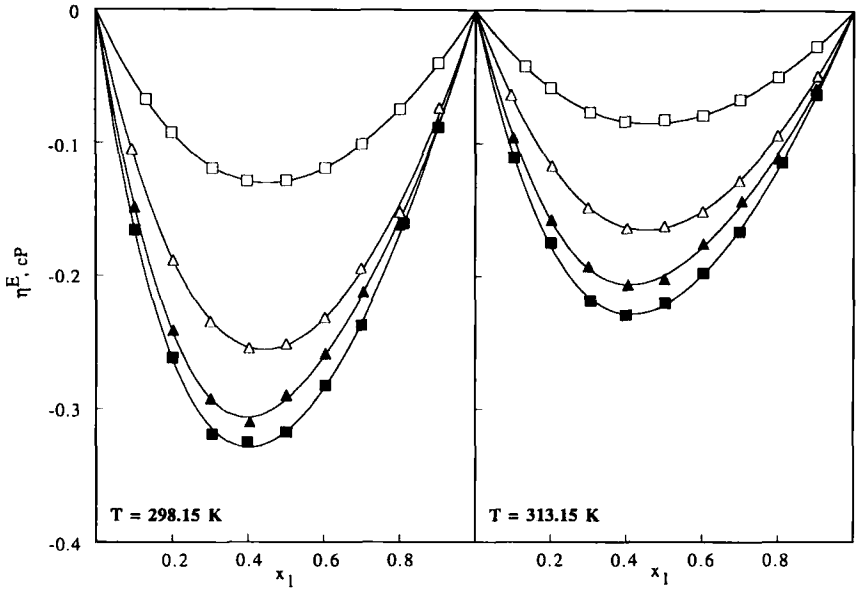

Fig. 2. Excess volumes, η^E, of cyclic ethers (1) + bromocyclohexane (2) at 298.15 and 313.15 K as a function of mole fraction x_1: tetrahydrofuran (△); tetrahydropyran (□); 2-methyl-tetrahydrofuran (▲); 2,5-dimethyl-tetrahydrofuran (■); (——) Redlich–Kister equations.

in absolute value in the sequence tetrahydropyran < tetrahydrofuran < 2-methyltetrahydrofuran < 2,5-dimethyltetrahydrofuran, although the values for tetrahydrofuran and tetrahydropyran are similar at 298.15 K.

In these mixtures the main factors which affect excess volumes are the breaking of the dipole–dipole interactions in the pure cyclic ethers by the bromocyclohexane and the specific Br–O interaction. The first of them yields a positive contribution to the resultant excess volume, while the Br–O interaction, where the oxygen atom is the donor atom [7] and the bromine atom is the acceptor atom, leads to negative excess volume. This explanation is corroborated by the fact that the excess volumes for the mixtures cyclohexane + tetrahydrofuran [8] and + tetrahydropyran [9] are both positive, while they are slightly negative when the cyclic hydrocarbon is replaced by the bromocyclohexane. The two mentioned effects are quite balanced in the mixtures containing tetrahydrofuran and tetrahydropyran but the negative contribution is stronger when the cyclic ethers are 2-methyltetrahydrofuran and especially, 2,5-dimethyltetrahydrofuran. These results seem to indicate that the donor ability of the oxygen atom is bigger in these two last compounds.

The excess viscosities are negative and decrease in absolute value as the temperature is increased. η^E values increase in absolute value in the sequence tetrahydropyran < tetrahydrofuran < 2-methyltetrahydrofuran < 2,5-dimethyltetrahydrofuran, although the values for 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran are similar. This viscosity behavior can be interpreted in a similar way to the V^E values, i.e., the breaking of dipole–dipole interactions in the pure cyclic ethers leads to a decrease in excess viscosity and the Br–O interaction leads to ae increase in η^E.

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