Excess Molar Volumes of Linear and Cyclic Ethers + Chloroethenes at 298.15 K

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Excess molar volumes V_m^E of binary liquid mixtures of trichloroethylene, C_2Cl_3H, and tetrachloroethylene, C_2Cl_4, with ethylene glycol monomethyl ether, $CH_3OC_2H_4OH$, diethylene glycol dimethyl ether, $CH_3(OC_2H_4)_2OCH_3$, and 1,4-dioxane, $[(OC_2H_4)_2]$, have been measured as a function of composition at 298.15 K. The measurements were carried out with a continuous-dilution dilatometer. The excess molar volumes V_m^E are positive over the entire range of composition for the systems trichloroethylene + ethylene glycol monomethyl ether and tetrachloroethylene + ethylene glycol monomethyl ether, +diethylene glycol dimethyl ether, and +1,4-dioxane and change sign from positive to negative for the remaining systems, trichloroethylene + diethylene glycol dimethyl ether and +1,4-dioxane. The measured excess volumes have been compared to our previous published data with an effort to assess the effects of replacing the hydroxyl hydrogen by methyl groups, of inserting oxyethylene groups, and of switching linear to cyclic ethers. These results are fitted to the Redlich−Kister equation to estimate the binary coefficients.

Introduction

Our interest lies in exploring the composition dependence of the excess molar volumes V_m^E of binary mixtures containing chloroethenes. In earlier papers (Pal and Singh, 1995, 1996), we reported measurements of the thermodynamic properties of mixtures of an alkoxyethanol with chloroethenes. The present paper reports the excess molar volumes V_m^E for binary mixtures of trichloroethylene (C_2Cl_3H) and tetrachloroethylene (C_2Cl_4) with ethylene glycol monomethyl ether ($CH_3OC_2H_4OH$), diethylene glycol dimethyl ether ($CH_3(OC_2H_4)_2OCH_3$), and 1,4-dioxane $[(OC_2H_4)_2]$ at 298.15 K. Our primary interest was to compare the excess molar volumes of the three systems [ethylene glycol monomethyl ether + chloroethenes, diethylene glycol monomethyl ether + chloroethenes (Pal and Singh, 1995), and triethylene glycol monomethyl ether + chloroethenes (Pal and Singh, 1996)]. We are also interested in comparing the excess molar volumes of diethylene glycol dimethyl ether + chloroethenes with those of our previous results for diethylene glycol monomethyl ether + chloroethenes (Pal and Singh, 1995).

Experimental Section

Materials. Reagent grade ethylene glycol monomethyl ether (S.D. Fine Chemicals, Bombay), diethylene glycol dimethyl ether (Spectrochem, Bombay), and 1,4-dioxane (E. Merck, Bombay) were further purified by standard methods (Riddick et al., 1986; Perrin et al., 1980). The manufacturer's estimates of the purity were, in each case, greater than mole fraction 0.99. Ethylene glycol monomethyl ether was dried over 4 Å molecular sieves and fractionally distilled. Diethylene glycol dimethyl ether was dried over anhydrous calcium chloride and fractionally distilled under reduced pressure from lithium aluminum hydroxide. These operations were carried out under a nitrogen atmosphere. 1,4-Dioxane was purified by fractional distillation over sodium wire under a nitrogen atmosphere and stored in the dark. The purities of the final samples were checked by measuring their densities with a double-armed pycnometer (Pal and Singh, 1994), and the relative error in densities at (298.15 ± 0.01) K is estimated to be $\leq 3 \times 10^{-4}$ g·cm^{-3}. The densities of the purified samples of ethylene glycol monomethyl ether, diethylene glycol dimethyl ether, and 1,4-dioxane at 298.15 K were (0.9602, 0.9390, and 1.0278) g·cm^{-3}, in good agreement with the available literature data (Riddick et al., 1986; Davis et al., 1990; Muhuri and Hazra, 1995; Sakurai, 1992; Francesconi and Comelli, 1995; Suri and Naorem, 1987; Defhlefsen and Hvidt, 1985; Skranc et al., 1995). The purities of these solvents were further ascertained by the chromatographic method, confirming the absence of other significant organic components. The water content, measured for each sample by Karl-Fischer titration, was always found to be less than 0.002 wt %. On the basis of this, the purity of the liquids was assessed to be better than 99.8 mol %. Trichloroethylene and tetrachloroethylene were the same as those used in earlier studies (Pal and Singh, 1995, 1996). Before measurements, all samples were stored over 4 Å molecular sieves and were partially degassed under vacuum.

Apparatus and Procedure. The excess molar volumes, which are accurate to ±0.003 cm^3·mol^{-1}, were measured by means of a continuous-dilution dilatometer similar to that described by Dickinson et al. (1975). Details of calibration, experimental setup, and operational procedure have been described previously (Pal and Singh, 1994; Pal et al., 1994). All the measurements were carried out in a thermostatically controlled, well-stirred water bath with the temperature controlled to ±0.01 K. The composition of each mixture was obtained from the measured apparent masses of the components with an accuracy of 1×10^{-4}. All masses were corrected for buoyancy. Each run covered just over half of the mole fraction range so as to give an overlap between two runs.

Results and Discussion

The experimental results of excess volume V_m^E for trichloroethylene + ethylene glycol monomethyl ether, +diethylene glycol dimethyl ether, and +1,4-dioxane and tetrachloroethylene + ethylene glycol monomethyl ether, +diethylene glycol dimethyl ether, and +1,4-dioxane at 298.15 K are presented in Tables 1 and 2 and are graphically represented as a function of the composition in Figures 1 and 2. The results for all the mixtures were

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Table 1. Excess Molar Volumes, V_m^E, for C_2Cl_3H (1) + $CH_3OC_2H_4OH$ (2), + $CH_3(OC_2H_4)_2OCH_3$ (2), and + $(OC_2H_4)_2$ (2) at 298.15 K

x_1	V_m^E/ cm^3·mol^{-1}	x_1	V_m^E/ cm^3·mol^{-1}	x_1	V_m^E/ cm^3·mol^{-1}
C_2Cl_3H (1) + $CH_3OC_2H_4OH$ (2)					
0.0533	0.004	0.3884	0.045	0.6667	0.116
0.0892	0.007	0.4667	0.062	0.7250	0.128
0.1061	0.013	0.5138	0.073	0.8070	0.135
0.1704	0.021	0.5235	0.075	0.8838	0.117
0.2717	0.030	0.5668	0.090	0.9333	0.081
0.3301	0.038	0.6089	0.103	0.9727	0.047
C_2Cl_3H (1) + $CH_3(OC_2H_4)_2OCH_3$ (2)					
0.0198	0.006	0.2934	−0.105	0.7029	−0.253
0.0398	0.009	0.3892	−0.162	0.7391	−0.236
0.0666	0.005	0.4501	−0.193	0.7914	−0.211
0.0997	−0.006	0.5294	−0.228	0.8330	−0.180
0.1298	−0.022	0.5825	−0.245	0.8693	−0.148
0.1842	−0.047	0.6406	−0.246	0.9143	−0.103
0.2049	−0.056	0.6567	−0.254	0.9582	−0.049
C_2Cl_3H (1) + $(OC_2H_4)_2$ (2)					
0.444	0.028	0.4030	0.051	0.7349	−0.036
0.0799	0.046	0.4398	0.041	0.7919	−0.042
0.1222	0.061	0.4727	0.030	0.8424	−0.045
0.1771	0.072	0.5416	0.007	0.8899	−0.036
0.2280	0.076	0.5605	0.005	0.9350	−0.026
0.2763	0.077	0.6245	−0.016	0.9620	−0.015
0.3267	0.068	0.6782	−0.026		
0.3667	0.060	0.7067	−0.031		

Table 2. Excess Molar Volumes, V_m^E, for C_2Cl_4 (1) + $CH_3OC_2H_4OH$ (2), + $CH_3(OC_2H_4)_2OCH_3$ (2), and + $(OC_2H_4)_2$ (2) at 298.15 K

x_1	V_m^E/ cm^3·mol^{-1}	x_1	V_m^E/ cm^3·mol^{-1}	x_1	V_m^E/ cm^3·mol^{-1}
C_2Cl_4 (1) + $CH_3OC_2H_4OH$ (2)					
0.0441	0.055	0.4174	0.365	0.7667	0.324
0.0867	0.107	0.4974	0.390	0.8090	0.295
0.1506	0.178	0.5680	0.398	0.8533	0.251
0.2077	0.235	0.6222	0.393	0.8855	0.213
0.2467	0.270	0.6467	0.387	0.9133	0.175
0.2842	0.301	0.6733	0.376	0.9401	0.131
0.3625	0.341	0.7177	0.354	0.9756	0.050
C_2Cl_4 (1) + $CH_3(OC_2H_4)_2OCH_3$ (2)					
0.0280	0.035	0.4296	0.316	0.7001	0.294
0.0733	0.083	0.4685	0.328	0.7485	0.268
0.1236	0.131	0.5215	0.334	0.8077	0.223
0.1768	0.170	0.5412	0.333	0.8650	0.164
0.2258	0.212	0.5534	0.332	0.9043	0.115
0.2811	0.248	0.5968	0.324	0.9450	0.073
0.3348	0.276	0.6608	0.310	0.9818	0.026
0.3858	0.295				
C_2Cl_4 (1) + $(OC_2H_4)_2$ (2)					
0.0333	0.042	0.3833	0.279	0.7767	0.226
0.0653	0.078	0.3949	0.282	0.8098	0.202
0.0993	0.114	0.4469	0.296	0.8439	0.177
0.1520	0.161	0.4950	0.302	0.8733	0.153
0.2030	0.199	0.5502	0.299	0.8989	0.131
0.2513	0.224	0.6173	0.287	0.9307	0.097
0.2911	0.247	0.6873	0.266	0.9615	0.057
0.3453	0.266	0.7259	0.252		

fitted to the equation (Redlich and Kister, 1948)

$$V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = x_1x_2\sum_{j=1}^{n}A_j(x_1 - x_2)^{j-1} \qquad (1)$$

where x_1 and x_2 are the mole fractions of chloroethene and ether molecules, respectively. The values of the coefficients, A_j, obtained by the method of least squares with all points weighted equally are given in Table 3 along with standard deviations $s(V_m^E)$. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard deviation with n:

$$s(V_m^E) = [\sum(V_{m,exptl}^E - V_{m,calcd}^E)^2/(n - p)]^{1/2} \qquad (2)$$

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

The excess volumes V_m^E for mixtures of diethylene glycol dimethyl ether and 1,4-dioxane with trichloroethylene and tetrachloroethylene are shown in Figure 1, together with those for diethylene glycol monomethyl ether with trichloroethylene and tetrachloroethylene (Pal and Singh, 1995).

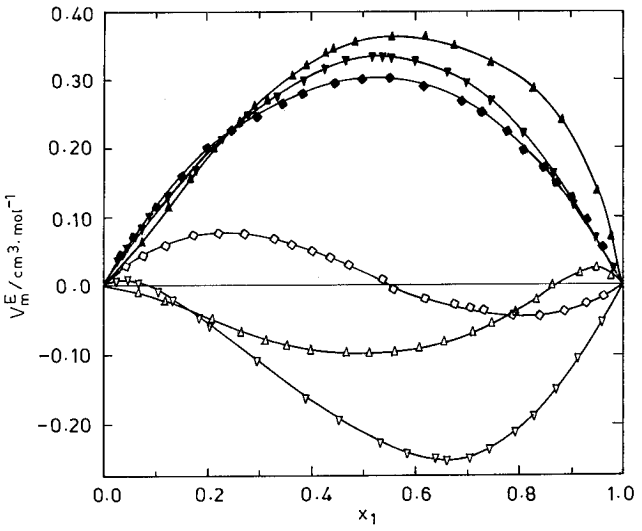

Figure 1. Excess molar volumes, V_m^E, of trichloroethylene (1) + diethylene glycol dimethyl ether (2) (▽) (this work), +diethylene glycol monomethyl ether (2) (△) (Pal and Singh, 1995), and +1,4-dioxane (2) (◇) (this work) and tetrachloroethylene (1) + diethylene glycol dimethyl ether (2) (▼) (this work), +diethylene glycol monomethyl ether (2) (▲) (Pal and Singh, 1995), and +1,4-dioxane (2) (◆) (this work) at 298.15 K. (—) Obtained using coefficients A_j of Table 3.

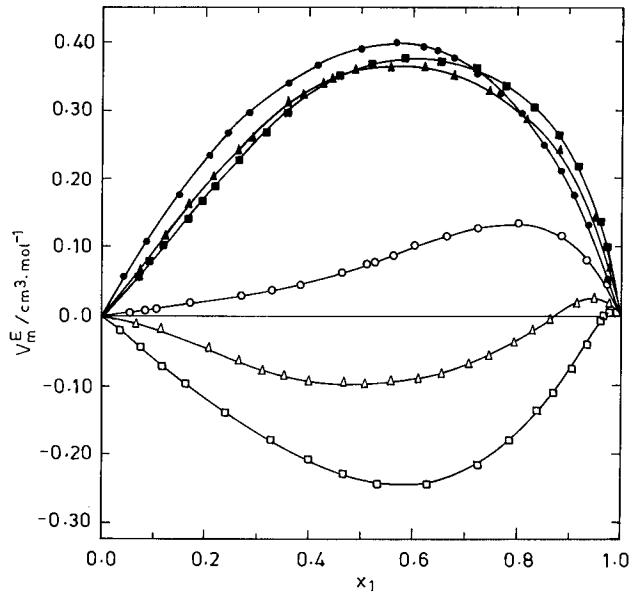

Figure 2. Excess molar volumes, V_m^E, of trichloroethylene (1) + ethylene glycol monomethyl ether (2) (○) (this work), +diethylene glycol monomethyl ether (2) (△) (Pal and Singh, 1995), and +triethylene glycol monomethyl ether (2) (□) (Pal and Singh, 1996) and tetrachloroethylene (1) + ethylene glycol monomethyl ether (2) (●) (this work), +diethylene glycol monomethyl ether (2) (▲) (Pal and Singh, 1995), and +triethylene glycol monomethyl ether (2) (■) (Pal and Singh, 1996) at 298.15 K. (—) Obtained using coefficients A_j of Table 3.

Table 3. Values of the Parameters of Eq 1 and Standard Deviations at 298.15 K

	A_1	A_2	A_3	A_4	A_5	$s(V_m^E)$/cm^3·mol^{-1}
C_2Cl_3H (1)						
$+CH_3OC_2H_4OH$ (2)	0.281	0.494	0.592	0.286		0.003
$+CH_3(OC_2H_4)_2OCH_3$ (2)	−0.862	−0.829	−0.055	0.100	0.529	0.003
$+(OC_2H_4)_2$ (2)	0.091	−0.618	0.030	0.010		0.002
C_2Cl_4 (1)						
$+CH_3OC_2H_4OH$ (2)	1.561	0.298	0.285	0.281		0.004
$+CH_3(OC_2H_4)_2OCH_3$ (2)	1.319	0.255	−0.033	−0.213		0.003
$+(OC_2H_4)_2$ (2)	1.190	0.064	0.228	0.052		0.003

There is a very obvious decrease in the magnitudes of the excess molar volumes with each substitution of a methyl group for a hydroxyl hydrogen in mixtures containing trichloroethylene, but with tetrachloroethylene the trend is opposite. This is related to the enhanced hydrophilic characteristics of the alkoxyethanol component in mixtures containing trichloroethylene. The excess volumes are positive in mixtures of 1,4-dioxane with tetrachloroethylene over the entire range of composition, and the curves are symmetric. An inversion in sign of V_m^E is observed from positive to negative in the trichloroethylene system. Figure 2 shows the composition dependence of excess volumes for mixtures of tri- and tetrachloroethylene with ethylene glycol monomethyl ether, $CH_3OC_2H_4OH$, diethylene glycol monomethyl ether, $CH_3(OC_2H_4)_2OH$, and triethylene glycol monomethyl ether, $CH_3(OC_2H_4)_3OH$ (Pal and Singh, 1996). V_m^E decreases with each addition of a $-OC_2H_4-$ group in the molecule of ethylene glycol monomethyl ether in the case of mixtures containing trichloroethylene. The behavior is similar to that of mixtures containing tetrachloroethylene at low x_1, and at higher x_1 the sequence is opposite. As expected, the V_m^E values for tri- and tetrachloroethylene + ethylene glycol monomethyl ether over the entire composition range at 303.15 and 313.15 K reported by Rao et al. (1992) lie above ours at 298.15 K. It is important to note that there is relatively little difference in the maximum values of V_m^E for the four linear and one cyclic diethers with tetrachloroethylene, while there is a large difference in the maximum values with trichloroethylene.

We suggested previously (Pal and Singh, 1995, 1996) that the volume behaviors of chloroethenes + *n*-alkoxyethanols or +1,4-dioxane are the result of several opposing effects accompanying the differences in the molecular size and the shape of the components, breaking of hydrogen bonds of the self-associated alkoxyethanols by the addition of tri- and tetrachloroethylene, and the complex formation between π-electrons of chloroethene and oxygen (−O−) in linear or in cyclic ethers.

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Literature Cited

Davis, M. I.; Douhéret, G.; Pal, A. Ultrasonic Speeds in (a 2-alkoxyethanol + water) at 298.15 K. *J. Chem. Thermodyn.* **1990**, *22*, 99−108.

Defhlefsen, C.; Hvidt, A. Densities and derived volume functions of binary mixture: (an ethylene glycol derivative + water) at 298.15 K. *J. Chem. Thermodyn.* **1985**, *17*, 193−199.

Dickinson, E.; Hunt, D. C.; McLure, I. A. Excess volumes of mixing of nearly spherical molecules 2. Mixtures containing cyclic dimethylsiloxanes. *J. Chem. Thermodyn.* **1975**, *7*, 731−740.

Francesconi, R.; Comelli, F. Excess Molar Volumes of Binary Mixtures Containing Diethyl Carbonate + Linear and Cyclic Ethers at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 512−514.

Muhuri, P. K.; Hazra, D. K. Density and Viscosity of Propylene Carbonate + 2-Methoxyethanol at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 582−585.

Pal, A.; Singh, Y. P. Excess molar volumes and apparent molar volumes of $[xH(CH_2)_nO(CH_2)_2O(CH_2)_2OH + (1-x)H_2O]$ at the temperature 298.15 K. *J. Chem. Thermodyn.* **1994**, *26*, 1063−1070.

Pal, A.; Singh, W. Excess Molar Volumes of 2-(2-Alkoxyethoxy)ethanols with Trichloroethylene and Tetrachloroethylene at 298.15 K and 308.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1130−1133.

Pal, A.; Singh, W. Excess Molar Volumes of 2-[2-(2-Alkoxyethoxy)-ethoxy]ethanols with Trichloroethylene and Tetrachloroethylene at 298.15 and 308.15 K. *J. Chem. Eng. Data* **1996**, *41*, 181−184.

Pal, A.; Singh, Y. P.; Singh, W. Excess Volumes and ultrasonic velocities of some amide + water systems at 298.15 K. *Indian J. Chem.* **1994**, *33A*, 1083−1087.

Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1980.

Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solution. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

Sakurai, M. Partial Molar Volumes for 1,4-Dioxane + Water. *J. Chem. Eng. Data* **1992**, *37*, 492−496.

Skranc, W.; Cibulka, I.; Hnědkovský, L. Excess Volumes of 1,4-Dioxane + Ethane-1,2-diol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 974−975.

Suri, S. K.; Naorem, H. Thermodynamic Studies of Binary Mixtures of Tetrahydrofuran with Some Oxygen- and Nitrogen-Containing Solvents: Molar Excess Volumes. *J. Chem. Eng. Data* **1987**, *32*, 462−464.

Venkatesulu, D.; Rao, M. V. P. Excess Volumes of 2-Alkoxyethanols with Trichloroethylene and Tetrachloroethylene. *J. Chem. Eng. Data* **1992**, *37*, 479−481.

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