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Excess Molar Volumes of 2-(2-Alkoxyethoxy)ethanols with Trichloroethylene and Tetrachloroethylene at 298.15 and 308.15 K

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The excess molar volumes for binary liquid mixtures of trichloroethylene, C_2Cl_3H, and tetrachloroethylene, C_2Cl_4, with 2-(2-methoxyethoxy)ethanol, $CH_3O(CH_2)_2O(CH_2)_2OH$, 2-(2-ethoxyethoxy)ethanol, $C_2H_5O(CH_2)_2O(CH_2)_2OH$, and 2-(2-butoxyethoxy)ethanol, $C_4H_9O(CH_2)_2O(CH_2)_2OH$, have been measured using a continuous-dilution dilatometer over the entire mole fraction range at 298.15 and 308.15 K. The excess volumes change sign for trichloroethylene and are positive for tetrachloroethylene with 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, and 2-(2-butoxyethoxy)ethanol over the whole composition range at both temperatures. The measured excess volume decreases as the alkyl chain length of the alkoxyethanol increases.

Introduction

As a part of our research program of determining excess thermodynamic functions of binary mixtures containing the oxy (−O−) and hydroxyl (−OH) functional groups (*1−5*), it is necessary to obtain values of excess volumes of some mixtures of an alkoxyethanol with an organic liquid. We report here the excess molar volumes for binary mixtures of C_2Cl_3H (1) + $H(CH_2)_\nu O(CH_2)_2O(CH_2)_2OH$ (2) and of C_2Cl_4 (1) + $H(CH_2)_\nu O(CH_2)_2O(CH_2)_2OH$ (2) for ν = 1, 2, and 4 over the whole mole fraction range at 298.15 and 308.15 K. To the best of our knowledge, there are no literature values for V^E_m available for these mixtures for comparison.

Experimental Section

Materials. Tetrachloroethylene (S.D. Fine Chemicals, GLC 99.9%) and trichloroethylene (S.D. Fine Chemicals, >99.5%, and S.R.L., Bombay, GC 99.5%) were purified by the standard methods (*6*). The purities of the final samples were checked by measuring their densities with a bicapillary pycnometer (*3*) at 303.15 K reproducible to within $\pm 3 \times 10^{-4}$ g·cm^{-3}. The densities of the purified samples of tetrachloroethylene and trichloroethylene at 303.15 K were 1.6064 and 1.4513 g·cm^{-3}, in good agreement with literature values (*6, 7*). 2-(2-Methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, and 2-(2-butoxyethoxy)ethanol were the same as used in earlier studies (*3*). Prior to measurements, all liquids were partially degassed and dried over 4A molecular sieves to reduce the water content.

Apparatus and Procedure. The measurements of excess volume were carried out in a continuous-dilution dilatometer similar to that described by Dickinson, Hunt, and McLure (*8*). Calibration and operational procedures have been described previously (*3, 9*). All the measurements were made in a thermostatically controlled, well-stirred water bath whose temperature was controlled to ±0.01 K. The measured excess volumes were accurate to ±0.003 cm^3·mol^{-1}. The composition of each mixture was obtained from the mass of the components with an accuracy of 2×10^{-4}. Corrections were made 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

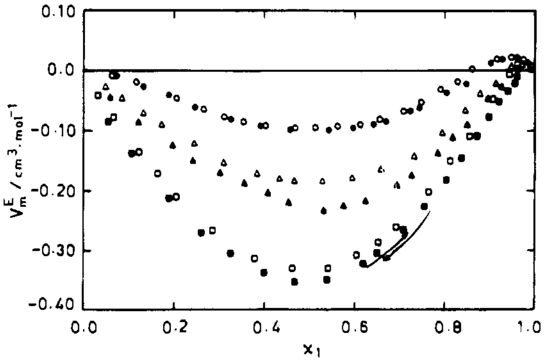

Figure 1. Excess volumes V^E_m for C_2Cl_3H (1) + $H(CH_2)_\nu O(CH_2)_2O(CH_2)_2OH$ (2) at 298.15 K (○, ν = 1; △, ν = 2; □, ν = 4) and at 308 15 K (●, ν = 1; ▲, ν = 2; ■, ν = 4).

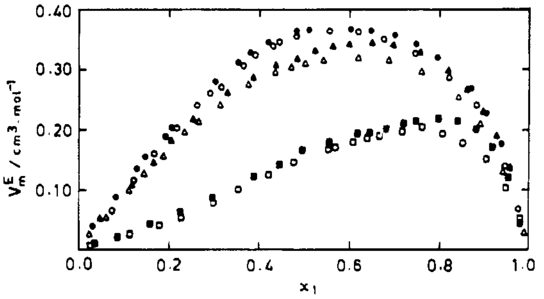

Figure 2. Excess volumes V^E_m for C_2Cl_4 (1) + $H(CH_2)_\nu O(CH_2)_2O(CH_2)_2OH$ (2) at 298.15 K (○, ν = 1; △, ν = 2; □, ν = 4) and at 308.15 K (●, ν = 1; ▲, ν = 2; ■, ν = 4).

The experimental results of excess volume for trichloroethylene + 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, and 2-(2-butoxyethoxy)ethanol and tetrachloroethylene + 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, and 2-(2-butoxyethoxy)ethanol at 298.15 and 308.15 K at various mole fractions are reported in Tables 1 and 2 and are graphically shown in Figures 1−4. The excess volumes are fitted to the Redlich−Kister equation (*10*):

$$V^E_m/(\mathrm{cm^3{\cdot}mol^{-1}}) = x_1x_2\sum_{j=0}^{n} a_j(x_1 - x_2)^j \tag{1}$$

The parameters a_j along with the standard deviations $s(V^E_m)$

$$s(V^E_m) = [\sum (V^E_{m,\mathrm{exptl}} - V^E_{m,\mathrm{calcd}})^2/(n - p)]^{1/2} \tag{2}$$

where n is the total number of data points and p the number of adjustable parameters a_j were evaluated by the

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Table 1. Excess Molar Volumes, V_m^E, for C_2Cl_3H (1) + $H(CH_2)_\nu O(CH_2)_2O(CH_2)_2OH$ (2) at 298.15 and 308.15 K

298.15 K				308.15 K			
x_1	V_m^E/ ($cm^3 \cdot mol^{-1}$)	x_1	V_m^E/ ($cm^3 \cdot mol^{-1}$)	x_1	V_m^E/ ($cm^3 \cdot mol^{-1}$)	x_1	V_m^E/ ($cm^3 \cdot mol^{-1}$)
C_2Cl_3H (1) + $CH_3O(CH_2)_2O(CH_2)_2OH$ (2)							
Run I							
0.0653	−0.007	0.3545	−0.085	0.0705	−0.009	0.3962	−0.092
0.1176	−0.020	0.4023	−0.091	0.1318	−0.027	0.4589	−0.099
0.2065	−0.047	0.4679	−0.095	0.1884	−0.041	0.5475	−0.099
0.2657	−0.065	0.5116	−0.094	0.2458	−0.059	0.6001	−0.094
0.3137	−0.077	0.6126	−0.090	0.3273	−0.082	0.6702	−0.084
Run II							
0.5633	−0.092	0.8345	−0.020	0.6427	−0.089	0.9078	0.013
0.6572	−0.081	0.8611	0.001	0.7273	−0.068	0.9304	0.017
0.7088	−0.065	0.9174	0.017	0.7434	−0.061	0.9600	0.020
0.7475	−0.053	0.9484	0.023	0.8050	−0.040	0.9876	0.009
0.7932	−0.038	0.9762	0.018	0.8501	−0.025	0.9899	0.007
C_2Cl_3H (1) + $H(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)							
Run I							
0.0467	−0.026	0.3194	−0.153	0.0569	−0.045	0.3552	−0.187
0.0843	−0.045	0.3838	−0.170	0.1225	−0.086	0.4096	−0.205
0.1333	−0.071	0.4333	−0.179	0.1970	−0.124	0.4545	−0.219
0.1739	−0.090	0.4685	−0.182	0.2429	−0.151	0.5341	−0.232
0.2450	−0.121	0.5965	−0.183	0.3026	−0.170	0.6237	−0.224
Run II							
0.5299	−0.183	0.8796	−0.040	0.5765	−0.224	0.8529	−0.090
0.6606	−0.165	0.9170	−0.020	0.6954	−0.190	0.9006	−0.047
0.7342	−0.144	0.9500	0.002	0.7268	−0.174	0.9236	−0.029
0.7970	−0.106	0.9714	0.008	0.7859	−0.137	0.9635	0.002
0.8467	−0.067	0.9916	0.002	0.8215	−0.111	0.9898	0.001
C_2Cl_3H (1) + $H(CH_2)_4O(CH_2)_2O(CH_2)_2OH$ (2)							
Run I							
0.0333	−0.040	0.2857	−0.266	0.0562	−0.085	0.3990	−0.338
0.0672	−0.078	0.3812	−0.312	0.1065	−0.137	0.4671	−0.352
0.1228	−0.135	0.4647	−0.331	0.1897	−0.212	0.5401	−0.349
0.1633	−0.170	0.5430	−0.328	0.2610	−0.271	0.6117	−0.321
0.2063	−0.209	0.6533	−0.285	0.3266	−0.305	0.7071	−0.264
Run II							
0.6077	−0.308	0.9069	−0.048	0.6497	−0.304	0.8997	−0.078
0.6944	−0.261	0.9446	−0.007	0.7571	−0.226	0.9222	−0.052
0.7688	−0.201	0.9624	0.006	0.8029	−0.182	0.9418	−0.035
0.8147	−0.151	0.9785	0.009	0.8394	−0.146	0.9554	−0.021
0.8574	−0.109	0.9927	0.003	0.8691	−0.110	0.9623	−0.010

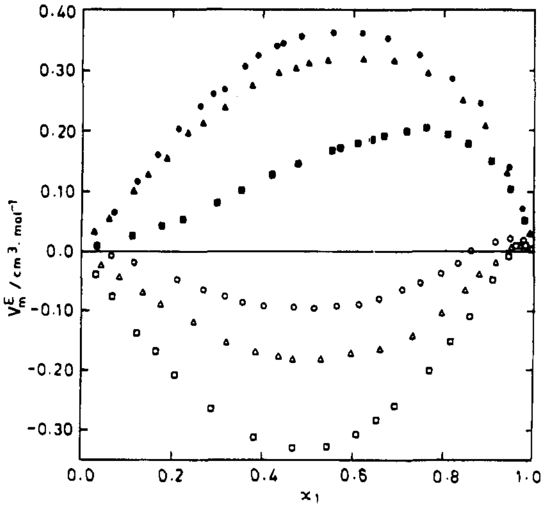

Figure 3. Excess volumes V_m^E for C_2Cl_3H (1) + $H(CH_2)_\nu O(CH_2)_2$-$O(CH_2)_2OH$ (2) (○, ν = 1; △, ν = 2; □, ν = 4) and for C_2Cl_4 (1) + $H(CH_2)_\nu O(CH_2)_2O(CH_2)_2OH$ (2) (●, ν = 1; ▲, ν = 2; ■, ν = 4) at 298.15 K.

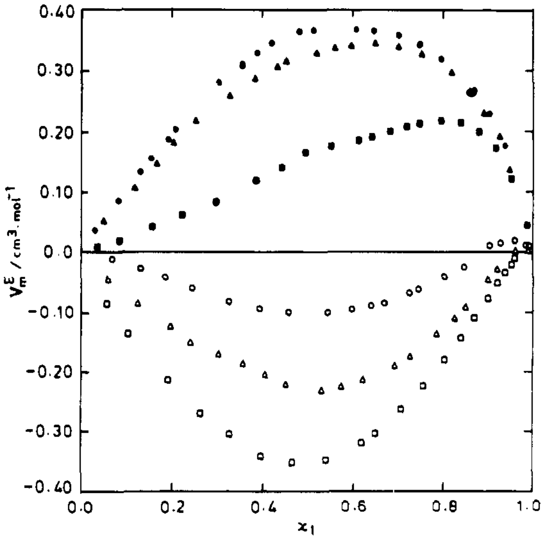

Figure 4. Excess volumes V_m^E for C_2Cl_3H (1) + $H(CH_2)_\nu O(CH_2)_2$-$O(CH_2)_2OH$ (2) (○, ν = 1; △, ν = 2; □, ν = 4) and for C_2Cl_4 (1) + $H(CH_2)_\nu O(CH_2)_2O(CH_2)_2OH$ (2) (●, ν = 1; ▲, ν = 2; ■, ν = 4) at 308.15 K.

method of least squares with all points weighted equally and are listed in Table 3.

Excess volume versus composition plots in Figures 1 and 2 show that V_m^E changes sign in mixtures of trichloroethylene and is positive for tetrachloroethylene with alkoxyethanols at both temperatures. Figure 1 shows that the excess volume for trichloroethylene is negative at lower

Table 2. Excess Molar Volumes, V_m^E, for C_2Cl_4 (1) + $H(CH_2)_vO(CH_2)_2O(CH_2)_2OH$ (2) at 298.15 and 308.15 K

298.15 K				308.15 K			
x_1	$V_m^E/(cm^3 \cdot mol^{-1})$	x_1	$V_m^E/(cm^3 \cdot mol^{-1})$	x_1	$V_m^E/(cm^3 \cdot mol^{-1})$	x_1	$V_m^E/(cm^3 \cdot mol^{-1})$
C_2Cl_4 (1) + $CH_3O(CH_2)_2O(CH_2)_2OH$ (2)							
Run I							
0.0755	0.065	0.2900	0.260	0.0348	0.039	0.2082	0.203
0.1235	0.118	0.3160	0.270	0.0849	0.088	0.3049	0.281
0.1686	0.160	0.3638	0.307	0.1320	0.134	0.3571	0.312
0.2129	0.203	0.3894	0.324	0.1559	0.155	0.3841	0.328
0.2635	0.241	0.4338	0.340	0.1917	0.188	0.4827	0.364
Run II							
0.4423	0.345	0.7476	0.326	0.4237	0.346	0.7502	0.342
0.4855	0.357	0.8211	0.288	0.5125	0.366	0.7989	0.320
0.5558	0.363	0.8830	0.245	0.6059	0.368	0.8693	0.268
0.6207	0.363	0.9474	0.139	0.6502	0.366	0.9026	0.228
0.6763	0.351	0.9767	0.070	0.7027	0.358	0.9377	0.176
C_2Cl_4 (1) + $H(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)							
Run I							
0.0251	0.024	0.2346	0.195	0.0496	0.050	0.3306	0.260
0.0618	0.053	0.2668	0.211	0.1201	0.107	0.3867	0.286
0.1142	0.098	0.3130	0.239	0.1667	0.145	0.4367	0.305
0.1446	0.125	0.3757	0.274	0.2045	0.180	0.4848	0.315
0.1884	0.156	0.4700	0.302	0.2545	0.217	0.5616	0.338
Run II							
0.4344	0.295	0.7605	0.294	0.5233	0.329	0.8201	0.297
0.5014	0.310	0.8415	0.251	0.6002	0.340	0.8600	0.265
0.5423	0.315	0.8902	0.208	0.6512	0.344	0.8954	0.230
0.6185	0.319	0.9390	0.130	0.7001	0.339	0.9266	0.189
0.6875	0.315	0.9904	0.028	0.7548	0.327	0.9512	0.135
C_2Cl_4 (1) + $H(CH_2)_4O(CH_2)_2O(CH_2)_2OH$ (2)							
Run I							
0.0324	0.008	0.3534	0.100	0.0356	0.009	0.3883	0.121
0.1122	0.025	0.4203	0.125	0.0845	0.019	0.4435	0.141
0.1774	0.041	0.4767	0.144	0.1558	0.043	0.4951	0.166
0.2248	0.053	0.5539	0.165	0.2235	0.063	0.5528	0.177
0.2977	0.079			0.2979	0.085	0.6429	0.192
Run II							
0.5664	0.170	0.8079	0.193	0.6147	0.186	0.8397	0.214
0.6079	0.179	0.8528	0.178	0.6816	0.200	0.8797	0.200
0.6380	0.184	0.9029	0.150	0.7193	0.209	0.9164	0.173
0.6659	0.191	0.9475	0.103	0.7468	0.212	0.9512	0.121
0.7156	0.197	0.9808	0.051	0.7959	0.218	0.9860	0.045
0.7580	0.204						

Table 3. Values of the Parameters of Eq 1 and Standard Deviations at 298.15 and 308.15 K

	T/K	a_0	a_1	a_2	a_3	a_4	a_5	$s(V_m^E)/(cm^3 \cdot mol^{-1})$
C_2Cl_3H (1)								
+ $CH_3O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	−0.3808	0.0190	0.1244	−0.0645	0.7186	0.5403	0.002
	308.15	−0.3965	0.0212	0.1145	−0.3259	0.6477	0.8542	0.004
+ $H(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	−0.7321	−0.0628	−0.0302	−0.1348	0.7418	0.7975	0.004
	308.15	−0.8966	−0.1897	0.1845	0.3692	0.2864	0.3590	0.004
+ $H(CH_2)_4O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	−1.3195	0.1220	0.1576	−0.3090	0.7604	1.1935	0.003
	308.15	−1.4063	0.1307	0.3663	−0.2099	0.0462	0.9691	0.003
C_2Cl_4 (1)								
+ $CH_3O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	1.4350	0.3860	0.0299	0.3539	0.6747	0.6422	0.004
	308.15	1.4613	0.3251	0.1447	0.9107	0.7786		0.002
+ $H(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	1.2296	0.2875	0.3557	0.9984	0.2313	−0.4623	0.004
	308.15	1.2998	0.4944	0.4326	0.4236	0.4426	0.3810	0.003
+ $H(CH_2)_4O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	0.6050	0.6092	0.2095	0.4743	0.5920		0.003
	308.15	0.6430	0.5861	0.1916	0.5807	1.0104	0.4055	0.003

values of x_1 and positive for higher values of x_1. Alkoxyethanols self-associate like alcohols. The presence of the etheric oxygen enhances the ability of the −OH group of the alkoxyethanols (*11*) to form hydrogen bonds with π-electrons of chloroethenes and hence result in a contraction in volume. Again, due to the electron-donating inductive effect of the alkyl group, the strength of bonding in alkoxyethanols increases with an increase in chain length. The behavior is consistent with that of the V_m^E for the alkoxyethanols with alkanes (*12*). Figure 2 shows that the addition of tetrachloroethylene appears to cause hydrogen bonds to break in alkoxyethanols, resulting in a positive contribution to the excess volume at both temperatures. The V_m^E values are strongly positive, smaller for the components with higher alkyl chain length, with the same sequence observed for H_m^E and $C_{p,m}^E$ of the alkoxyethanols with solvents like alkanes and ethers (*12*, *13*). The fairly high dipole moment in trichloroethylene in comparison to tetrachloroethylene also results in a negative contribution to V_m^E with alkoxyethanols, which have a moderate polarity. The behavior for mixtures of tri- and tetrachloroethylene with 2-(2-alkoxyethoxy)ethanols is similar to that with 2-alkoxyethanols (7) except for 2-methoxyethanol, being large negative and less unsymmetrical with trichloroethylene and positive and symmetrical with tetrachloroethylene.

A further comparison of Figures 3 and 4 at 298.15 and 308.15 K suggests that the temperature coefficient $(dV^E/dT)_P$ is positive for mixtures with tetrachloroethylene and negative for mixtures with trichloroethylene over the whole mole fraction range. The algebraic values of V_m^E for all the binary systems with trichloroethylene and with tetrachloroethylene are in the order 2-(2-methoxyethoxy)ethanol > 2-(2-ethoxyethoxy)ethanol > 2-(2-butoxyethoxy)ethanol.

Literature Cited

(1) Douhéret, G.; Pal, A. Dielectric Constants and Densities of Aqueous Mixtures of 2-Alkoxyethanols at 25 °C. *J. Chem. Eng. Data* **1988**, *33*, 40.

(2) Douhéret, G.; Pal, A.; Davis, M. I. Excess Thermodynamic Properties of some 2-Alkoxyethanol-Water Systems. *J. Chem. Soc., Faraday Trans. 1* **1988**, *85*, 2723.

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

(4) Pal, A.; Halder, P. N.; Singh, Wazir Excess molar volumes and apparent molar volumes of water + polyethyleneglycol mixtures at 303.15 and 308.15 K. *Indian J. Chem.* **1994**, *33A*, 154.

(5) Pal, A.; Singh, Wazir Excess molar volumes of binary mixed solvents containing 2-ethoxyethanol and ethylene glycol, propylene glycol, glycerol and cyclohexane at 298.15 K. *Indian J. Chem.* **1995**, *34A*, 389.

(6) Riddick, J. A.; Bunger, W. B.; Sakana, T. K. Organic Solvents. *Techniques of Chemistry*, 4th ed.; John Wiley and Sons: New York, 1986; Vol. II.

(7) Venkatesulu, D.; Rao, M. V. P. Excess Volumes of 2-Alkoxyethanols with Trichloroethylene and Tetrachloroethylene. *J. Chem. Eng. Data* **1992**, *37*, 402.

(8) 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.

(9) Pal, A.; Singh, Y. P.; Singh, Wazir Excess volumes and ultrasonic velocities of some amide + water systems at 298.15 K. *Indian J. Chem.* **1994**, *33A*, 1083.

(10) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345.

(11) Buckley, P.; Brochu, M. Microwave Spectrum, Dipole Moment, and Intramolecular Hydrogen bond of 2-Methoxyethanol. *Can. J. Chem.* **1972**, *50*, 1149.

(12) Barbes, B.; Garcia, I.; González, J. A.; Cobos, J. C.; Casanova, C. J. Excess properties of (an n-alkoxyethanol + an organic solvent) VI. V_m^E $[xCH_3(CH_2)_{\nu-1}O(CH_2)_2O(CH_2)_2OH + (1-x)C_6H_5CH_3]$ for $\nu = 1, 2,$ and 4 at the temperature 298.15 K. *J. Chem. Thermodyn.* **1994**, *26*, 791.

(13) Cobos, J. C.; Casanova, C.; Roux-Desgranges, G.; Grolier, J.-P. E. Excess properties of mixtures of some n-alkoxyethanol with organic solvents II. V_m^E and $C_{p,m}^E$ with di-n-butylether at 298.15 K. *J. Chem. Thermodyn.* **1987**, *19*, 791.

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