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

Amalendu Pal* and Wazir Singh

Department of Chemistry, University of Kurukshetra, Kurukshetra 132 119, India

The excess molar volumes for binary mixtures of trichloroethylene, C_2Cl_3H, and tetrachloroethylene, C_2Cl_4, with 2-[2-(2-methoxyethoxy)ethoxy]ethanol, $CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$, 2-[2-(2-ethoxyethoxy)ethoxy]ethanol, $C_2H_5O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$, and 2-[2-(2-butoxyethoxy)ethoxy]ethanol, $C_4H_9O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$, have been measured as a function of composition at 298.15 and 308.15 K. The measurements were determined using a continuous-dilution dilatometer. The excess volumes are negative for trichloroethylene mixtures with the exception of 2-[2-(2-methoxyethoxy)ethoxy]ethanol and are positive for tetrachloroethylene + 2-[2-(2-methoxyethoxy)ethoxy]ethanol, + 2-[2-(2-ethoxyethoxy)ethoxy]ethanol, and + 2-[2-(2-butoxyethoxy)ethoxy]ethanol over the whole composition range at both temperatures. The excess volumes decrease in magnitude as the alkyl chain length of the alkoxyethanol increases. A qualitative interpretation of the results is presented.

Introduction

Our recent research has been concerned with the measurement, analysis, and interpretation of the excess thermodynamic properties of binary mixtures containing the oxy (−O−) and hydroxy (−OH) functional groups (Douhéret and Pal, 1988; Douhéret et al., 1989; Pal and Singh, 1994, 1995a,d). Our aim is to provide the information required for the characterization of the molecular interactions of these groups. In our previous paper (Pal and Singh, 1995b) we studied the excess molar volumes 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 at 298.15 and 308.15 K. In continuation of these investigations of mixtures of an alkoxyethanol with an organic solvent, in the present paper we report the excess molar volumes for binary mixtures of C_2Cl_3H (1) + $H(CH_2)_\nu O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2) and of C_2Cl_4 (1) + $H(CH_2)_\nu O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2) for ν = 1, 2, and 4 at 298.15 and 308.15 K. No literature results are available for these mixtures.

Experimental Section

Materials. Materials were the same as used in earlier studies (Pal and Singh, 1995a,b). Before the measurements, all liquids were stored over molecular sieves type 4A to reduce the water content, and were partially degassed under vacuum.

Apparatus and Procedure. Excess molar volumes were measured directly by means of a continuous-dilution dilatometer described elsewhere (Dickinson et al., 1975). Details of its calibration, experimental setup, and operational procedure have been described previously (Pal and Singh, 1994, 1995c). The measured excess volumes were reproducible to ±0.003 $cm^3 \cdot mol^{-1}$. All the measurements were carried out in a thermostatistically controlled, well-stirred water bath whose temperature was controlled to ±0.01 K. The composition of each mixture was obtained with an accuracy of 2×10^{-4} from the measured apparent masses of the components. Corrections were made for buoyancy. Each run covered just over half of the mole fraction range so as to give an overlap between the two runs.

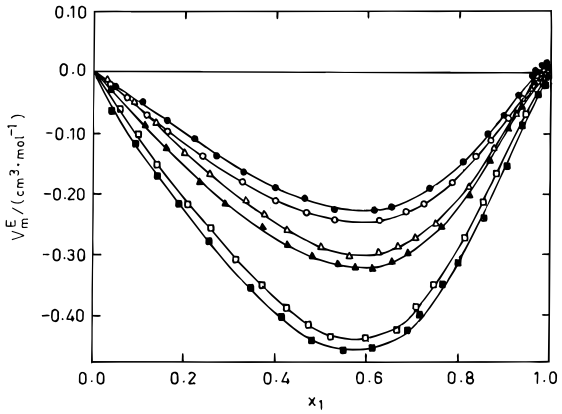

Figure 1. Excess volumes V_m^E for C_2Cl_3H (1) + $H(CH_2)_\nu O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2) at 298.15 K (○, ν = 1; △, ν = 2; □, ν = 4) and at 308.15 K (●, ν = 1; ▲, ν = 2; ■, ν = 4). Solid curves were calculated from eq 1 using coefficients a_j of Table 3.

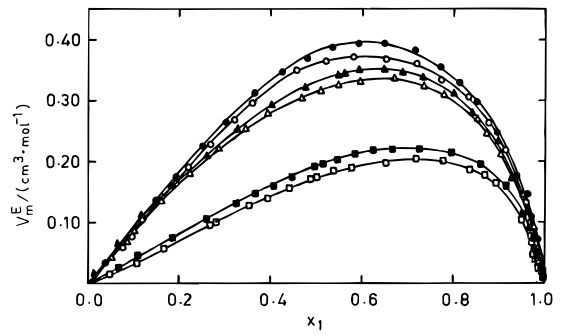

Figure 2. Excess volumes V_m^E for C_2Cl_4 (1) + $H(CH_2)_\nu O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2) at 298.15 K (○, ν = 1; △, ν = 2; □, ν = 4) and at 308.15 K (●, ν = 1; ▲, ν = 2; ■, ν = 4). Solid curves were calculated from eq 1 using coefficients a_j of Table 3.

Results and Discussion

The experimental results of excess volume for trichloroethylene + 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]ethanol, and 2-[2-(2-butoxyethoxy)-

* To whom correspondence should be addressed.

0021-9568/96/1741-0181$12.00/0

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

298.15 K				308.15 K			
x_1	V_m^E/(cm³·mol⁻¹)	x_1	V_m^E/(cm³·mol⁻¹)	x_1	V_m^E/(cm³·mol⁻¹)	x_1	V_m^E/(cm³·mol⁻¹)
			C_2Cl_3H (1) + $CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)				
			Run I				
0.0367	−0.020	0.3985	−0.209	0.0444	−0.022	0.3986	−0.189
0.0725	−0.042	0.4667	−0.229	0.1065	−0.050	0.4633	−0.207
0.1167	−0.070	0.5300	−0.242	0.1630	−0.079	0.5288	−0.225
0.1621	−0.095	0.6283	−0.243	0.2235	−0.107	0.6165	−0.225
0.2382	−0.138	0.7268	−0.214	0.2727	−0.135	0.7362	−0.189
0.3250	−0.179			0.3320	−0.163		
			Run II				
0.6867	−0.229	0.9358	−0.039	0.6517	−0.220	0.9588	−0.007
0.7867	−0.179	0.9653	−0.004	0.8104	−0.144	0.9688	0.001
0.8361	−0.136	0.9733	0.002	0.8630	−0.101	0.9767	0.009
0.8693	−0.110	0.9839	0.006	0.8979	−0.069	0.9894	0.014
0.9053	−0.075	0.9933	0.003	0.9301	−0.036	0.9936	0.009
			C_2Cl_3H (1) + $H(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)				
			Run I				
0.0264	−0.011	0.3351	−0.212	0.0361	−0.081	0.3701	−0.255
0.0883	−0.049	0.3726	−0.234	0.1136	−0.085	0.4275	−0.284
0.1371	−0.085	0.4254	−0.260	0.1623	−0.124	0.4822	−0.304
0.1988	−0.132	0.4971	−0.287	0.2344	−0.180	0.5409	−0.318
0.2543	−0.165	0.6247	−0.297	0.2873	−0.216	0.6119	−0.322
			Run II				
0.5612	−0.302	0.8771	−0.124	0.5751	−0.320	0.8698	−0.144
0.6662	−0.286	0.9199	−0.068	0.6522	−0.314	0.9073	−0.092
0.7066	−0.272	0.9534	−0.028	0.6902	−0.296	0.9335	−0.058
0.7512	−0.249	0.9752	−0.009	0.7613	−0.254	0.9634	−0.015
0.8220	−0.189	0.9854	−0.003	0.8223	−0.203	0.9883	−0.003
			C_2Cl_3H (1) + $H(CH_2)_4O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)				
			Run I				
0.0571	−0.060	0.3700	−0.351	0.0462	−0.060	0.3477	−0.354
0.0980	−0.103	0.4225	−0.387	0.0933	−0.115	0.4104	−0.402
0.1413	−0.151	0.4733	−0.414	0.1402	−0.168	0.4805	−0.439
0.2062	−0.214	0.5177	−0.432	0.1864	−0.215	0.5487	−0.456
0.2567	−0.257	0.6657	−0.422	0.2533	−0.277	0.6865	−0.422
0.3125	−0.308						
			Run II				
0.5997	−0.435	0.8824	−0.164	0.6139	−0.451	0.9037	−0.153
0.7066	−0.387	0.9437	−0.068	0.7132	−0.397	0.9388	−0.086
0.7461	−0.349	0.9760	−0.016	0.7639	−0.350	0.9684	−0.036
0.8143	−0.272	0.9896	−0.002	0.7986	−0.312	0.9829	−0.018
0.8533	−0.212			0.8550	−0.239	0.9914	−0.007

ethoxy]ethanol and tetrachloroethylene + 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-ethanol, and 2-[2-(2-butoxyethoxy)ethanol]ethanol at 298.15 and 308.15 K are presented as a function of mole fraction in Tables 1 and 2 and are graphically shown in Figures 1 and 2. The results for all the mixtures are fitted to the Redlich−Kister equation

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

In each case, the optimum number of coefficients a_j was ascertained from an examination of the variation of the standard deviation with n:

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

The values adopted for the coefficients a_j and the standard deviation s associated with the use of eq 2 are summarized in Table 3.

Excess volume versus composition plots in Figure 1 show that V_m^E is negative for mixtures of trichloroethylene with 2-[2-(2-ethoxyethoxy)ethoxy]ethanol and 2-[2-(2-butoxyethoxy)ethoxy]ethanol and is mostly negative with 2-[2-(2-methoxyethoxy)ethoxy]ethanol at lower values of x_1 and positive for higher values of x_1 at both temperatures. For the mixtures of tetrachloroethylene with alkoxyethanols at both temperatures as shown in Figure 2, V_m^E is positive over the whole mole fraction range. V_m^E decreases as the alkyl chain length of the alkoxyethanol increases. Alkoxyethanols exist as an associated structure like the alcohols (Franks and Ives, 1966; Cobos and Casanova, 1987) in the liquid state, and the association may be due to intramolecular hydrogen bond formation between the etheric oxygen and the −OH group. The presence of the etheric oxygen enhances the ability of the −OH group to form hydrogen bonds. When the mixture is formed, different effects must be considered: The hydrogen bond of the self-associated alkoxyethanols can be broken and new hydrogen bonds formed between π-electrons of chloroethenes and oxygen (−O−) in alkoxyethanols. The observed excess volume results from the above two major effects. Again, due to the electron-donating inductive effect of the alkyl group, the strength of bonding with trichloroethylene increases as the aliphatic chain length of the n-alkoxyethanol in each homologous series (Pal and Singh, 1995b; Vankatesulu and Rao, 1992) increases. For tetrachloroethylene the excess volumes are positive, smaller for the components with higher alkyl chain length, with the same sequence observed in the other two homologous series but with less significant change. On the other hand, it is important to note which dipole moment of trichloroethylene

Table 2. Excess Molar Volumes, V_m^E, for C_2Cl_4 (1) + $H(CH_2)_4O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2) at 298.15 and 308.15 K

298.15 K				308.15 K			
x_1	V_m^E/(cm³·mol⁻¹)	x_1	V_m^E/(cm³·mol⁻¹)	x_1	V_m^E/(cm³·mol⁻¹)	x_1	V_m^E/(cm³·mol⁻¹)
			C_2Cl_4 (1) + $CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)				
			Run I				
0.0733	0.062	0.2200	0.191	0.0377	0.033	0.3665	0.313
0.0933	0.078	0.2667	0.230	0.1535	0.134	0.4270	0.348
0.1200	0.103	0.3200	0.269	0.1937	0.175	0.4796	0.369
0.1633	0.139	0.3601	0.297	0.2527	0.225	0.5348	0.387
0.1934	0.165	0.5206	0.364	0.3038	0.264	0.6516	0.394
			Run II				
0.4574	0.350	0.8301	0.305	0.5935	0.394	0.8964	0.248
0.5827	0.373	0.8776	0.262	0.7164	0.385	0.9377	0.175
0.6515	0.369	0.9133	0.217	0.7723	0.354	0.9584	0.146
0.7215	0.361	0.9600	0.137	0.8141	0.330	0.9746	0.108
0.7762	0.334	0.9739	0.098	0.8522	0.297	0.9858	0.070
						0.9971	0.024
			C_2Cl_4 (1) + $H(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)				
			Run I				
0.0508	0.041	0.2874	0.220	0.0150	0.014	0.3274	0.253
0.0867	0.071	0.3468	0.252	0.0707	0.062	0.4036	0.291
0.1033	0.084	0.3910	0.275	0.1283	0.107	0.4761	0.320
0.1621	0.137	0.4659	0.303	0.1832	0.159	0.5496	0.340
0.2236	0.179	0.5471	0.324	0.2592	0.207	0.5897	0.348
			Run II				
0.5067	0.315	0.8509	0.271	0.5587	0.343	0.8423	0.277
0.5953	0.331	0.8733	0.244	0.6484	0.351	0.8925	0.227
0.6728	0.334	0.9044	0.210	0.6953	0.345	0.9315	0.173
0.7333	0.324	0.9511	0.143	0.7311	0.335	0.9676	0.089
0.7770	0.311	0.9764	0.089	0.8016	0.310	0.9836	0.045
			C_2Cl_4 (1) + $H(CH_2)_4O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)				
			Run I				
0.0460	0.013	0.3541	0.127	0.0667	0.024	0.3686	0.148
0.1067	0.033	0.3933	0.141	0.1105	0.045	0.4067	0.161
0.1658	0.058	0.4400	0.157	0.1869	0.074	0.4467	0.175
0.2667	0.094	0.4979	0.176	0.2581	0.106	0.5116	0.196
0.2800	0.101			0.3227	0.130		
			Run II				
0.4877	0.173	0.9686	0.080	0.4969	0.192	0.9733	0.075
0.5367	0.187	0.9731	0.071	0.5452	0.203	0.9785	0.059
0.5763	0.192	0.9784	0.054	0.5801	0.212	0.9831	0.049
0.6521	0.199	0.9794	0.048	0.6267	0.218	0.9866	0.042
0.7169	0.206	0.9825	0.045	0.6657	0.220	0.9889	0.037
0.7803	0.202	0.9872	0.037	0.7246	0.221	0.9919	0.028
0.8351	0.188	0.9904	0.028	0.7950	0.215	0.9953	0.023
0.8667	0.179	0.9958	0.017	0.8566	0.194	0.9967	0.019
0.8914	0.165	0.9970	0.016	0.9132	0.162	0.9979	0.012
0.9520	0.105	0.9991	0.006	0.9533	0.107		

Table 3. Values of the Parameters of Eq 1 and Standard Deviations $s(V_m^E)$ at 298.15 and 308.15 K

	T/K	a_1	a_2	a_3	a_4	a_5	a_6	$s(V_m^E)$/(cm³·mol⁻¹)
C_2Cl_3H (1)								
+ $CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	−0.9382	−0.3111	−0.1720	−0.3243	0.7950	1.0387	0.005
	308.15	−0.8643	−0.3130	−0.0319	−0.4958	0.7066	1.3346	0.006
+ $H(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	−1.1398	−0.5255	−0.0611	0.1097	0.8395	0.5393	0.004
	308.15	−1.2320	−0.4665	−0.1419	−0.0328	0.8223	0.8082	0.004
+ $H(CH_2)_4O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	−1.6961	−0.6830	0.1994	0.5779	0.5745	0.3004	0.004
	308.15	−1.7734	−0.5965	0.1522	0.2045	0.3092	0.6008	0.005
C_2Cl_4 (1)								
+ $CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	1.4499	0.5685	−0.0856	0.2595	1.0044	0.8702	0.004
	308.15	1.5191	0.7247	−0.0813	−0.2509	0.9872	1.3868	0.009
+ $H(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	1.2568	0.6075	0.3213	−0.1866	0.5731	1.1730	0.005
	308.15	1.3171	0.6125	0.3357	0.1715	0.4050	0.4215	0.003
+ $H(CH_2)_4O(CH_2)_2O(CH_2)_2O(CH_2)_2OH$ (2)	298.15	0.7049	0.5591	0.0919	−0.0605	0.7539	0.9242	0.003
	308.15	0.7718	0.5950	0.1201	−0.1944	0.8091	1.1340	0.004

is fairly high in comparison to that of tetrachloroethylene, resulting in a negative contribution to V_m^E with moderately polar solvents, *n*-alkoxyethanols.

The algebraic values of V_m^E for all the binary systems with trichloroethylene and with tetrachloroethylene are in the order 2-[2-(2-methoxyethoxy)ethoxy]ethanol > 2-[2-(2-ethoxyethoxy)ethoxy]ethanol > 2-[2-(2-butoxyethoxy)ethoxy]-ethanol.

A further comparison of Figures 1 and 2 at 298.15 and 308.15 K reveals that the temperature coefficient $(dV^E/dT)_p$ is positive for mixtures of tetrachloroethylene with 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]ethanol, and 2-[2-(2-butoxyethoxy)ethoxy]ethanol and trichloroethylene with 2-[2-(2-methoxyethoxy)ethoxy]-ethanol, and is negative for mixtures of trichloroethylene with 2-[2-(2-ethoxyethoxy)ethoxy]ethanol and 2-[2-(2-bu-

toxyethoxy)ethoxy]ethanol over the entire mole fraction range.

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Received for review July 31, 1995. Accepted October 30, 1995.[⊗] The authors are highly thankful to the Chairman, Department of Chemistry, Kurukshetra University for providing laboratory facilities. W.S. is also thankful to the Council of Scientific and Industrial Research, New Delhi, for awarding a Senior Research Fellowship.

JE9501898

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1995.