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Excess Molar Volumes of Ethyl Formate or Ethyl Acetate + 1-Chloroalkane at 298.15 K

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Excess molar volumes at 298.15 K of ethyl formate or ethyl acetate with 1-chloroalkanes (from C_5 to C_8) were calculated indirectly from densities. The V_m^E values were positive over the concentration range, increasing, for any one ester, with the length of the chain of the 1-chloroalkane and being smaller for the acetate than for ethyl formate.

Introduction

In order to understand the effect caused by the structure of compounds on the thermodynamic properties of solutions, systematic information on the behavior of substances with different structural characteristics is required. The literature includes several studies of the behavior of different families carrying some of the compounds studied here, such as those of chloroalkane + *n*-alkane (*1*), chloroalkane + 1-alkanol (*1*), ester + *n*-alkane (*2*, *3*), and ester + 1-alkanol (*4*, *5*) by means of different thermodynamic functions. However, few data are available for the systems ester + chloroalkane. This work presents excess molar volume data for the binary mixtures of ethyl formate and ethyl acetate with 1-ClC_nH_{2n+1} (n = 5, 6, 7, 8) at a constant temperature of 298.15 K, as part of the study in order to observe the interaction of the carbonyl group of the ester $\rangle C{=}O$ with other nonelectrolyte liquids containing structural groups such as CH_2, OH, and Cl.

Experimental Section

The materials used in this work, together with the specifications given by the manufacturer, are listed in Table I. All the products were used without further purification except the ethyl formate which was first washed with 2N sodium carbonate in order to remove the acid material, then stirred with calcium chloride for several hours to extract the ethyl alcohol and, finally, dried with potassium carbonate and distilled in a rectification column with a height equivalent to 120 theoretical plates. The final purity proved to be above 99 mol % verified by gas chromatography. However, before use, all the products were degassed in vacuo and dried with a molecular sieve, Type 4A, from Fluka. The experimental values and those taken from the literature for the refractive index and density of each of the substances chosen in this work are given in Table I. The agreement between the experimentally determined values and those found in the literature was considered to be satisfactory, since the greatest deviation found was smaller than 0.1%.

Excess volumes were determined from the density values of the mixtures, previously prepared by weighing. Densities were measured with an accuracy of ±0.01 kg·m^{-3} with an Anton Paar DMA-55 vibrating tube densimeter. Before each series of measurements, the apparatus was calibrated at atmospheric pressure by using bidistilled and degassed water and *n*-nonane, as recommended by the authors in an earlier work (*9*). The samples were thermostated in the densimeter cell at ±0.01 K using a Heto Birkeroad ultrathermostat together with a Anton Paar digital thermometer, Model DT 100-30. The mean error in the V_m^E was smaller than ±0.0003 cm^3·mol^{-1}.

Table I. Materials Employed and Their Characteristics at 298.15 K

		n_D		ρ, kg·m^{-3}	
material	supplier and specificns	expt	lit.	expt	lit.
ethyl formate	Aldrich >97 mol %	1.3576	1.35774 (6)[a]	915.87	916.03 (6)[a]
ethyl acetate	Fluka, puriss p.a. >99.5 mol %	1.3701	1.36979 (6)	894.34	894.55 (6)
1-chloropentane	Fluka, puriss >99 mol %	1.4099	1.4100 (6)	876.92	876.9 (6)
1-chlorohexane	Fluka, puriss >99 mol %	1.4174	1.4179 (8)[a]	873.33	874.5 (7)
1-chloroheptane	Alfa, >99 mol %	1.4232	1.4235 (7)[a]	870.56	871.5 (7)
1-chlorooctane	Fluka, >98 mol %	1.4280	1.4278 (7)[a]	868.65	869.5 (7)

[a] Value calculated by using the data shown in the mentioned reference.

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Table II. Molar Excess Volumes for (x)Ester + (1 − x)1-Chloroalkane Determined from Densities at 298.15 K

x	V^E_m/ $cm^3 \cdot mol^{-1}$	x	V^E_m/ $cm^3 \cdot mol^{-1}$	x	V^E_m/ $cm^3 \cdot mol^{-1}$
$xHCO_2C_2H_5 + (1 - x)C_5H_{11}Cl$					
0.042 17	0.0913	0.448 61	0.5853	0.733 30	0.4918
0.099 32	0.2008	0.483 38	0.5951	0.776 47	0.4437
0.146 88	0.2835	0.554 79	0.5959	0.850 39	0.3317
0.214 13	0.3868	0.612 58	0.5816	0.897 85	0.2448
0.280 60	0.4658	0.645 93	0.5636	0.934 93	0.1619
0.332 18	0.5164	0.688 07	0.5343	0.980 83	0.0520
$xHCO_2C_2H_5 + (1 - x)C_6H_{13}Cl$					
0.048 13	0.1110	0.564 56	0.6609	0.868 26	0.3527
0.071 71	0.1595	0.655 18	0.6287	0.906 06	0.2701
0.166 97	0.3369	0.723 66	0.5733	0.937 14	0.1901
0.217 01	0.4158	0.762 32	0.5285	0.963 89	0.1137
0.314 53	0.5402	0.781 61	0.5033	0.981 62	0.0589
0.399 83	0.6129	0.785 48	0.5001	0.990 83	0.0305
0.486 53	0.6551	0.821 66	0.4414		
$xHCO_2C_2H_5 + (1 - x)C_7H_{15}Cl$					
0.054 78	0.1279	0.438 12	0.6798	0.741 65	0.6120
0.102 18	0.2271	0.515 02	0.7106	0.815 72	0.5020
0.167 40	0.3521	0.566 17	0.7149	0.850 11	0.4367
0.198 36	0.4056	0.603 00	0.7074	0.911 35	0.2925
0.259 23	0.4972	0.685 10	0.6659	0.941 63	0.2022
0.331 33	0.5880	0.712 76	0.6420	0.982 82	0.0649
0.375 44	0.6295				
$xHCO_2C_2H_5 + (1 - x)C_8H_{17}Cl$					
0.057 38	0.1311	0.429 12	0.7109	0.737 97	0.6742
0.110 74	0.2495	0.464 42	0.7333	0.768 15	0.6349
0.149 11	0.3283	0.480 54	0.7414	0.828 36	0.5338
0.196 16	0.4149	0.543 20	0.7627	0.909 40	0.3332
0.257 39	0.5170	0.573 15	0.7650	0.937 88	0.2424
0.316 34	0.5986	0.627 35	0.7546	0.983 65	0.0710
0.375 92	0.6644	0.663 81	0.7400		
$xH_3CCO_2C_2H_5 + (1 - x)C_5H_{11}Cl$					
0.030 88	0.0522	0.395 33	0.4484	0.674 39	0.4308
0.064 32	0.1081	0.440 70	0.4649	0.741 55	0.3819
0.102 02	0.1644	0.503 29	0.4767	0.809 31	0.3123
0.186 95	0.2776	0.560 47	0.4741	0.882 86	0.2113
0.277 82	0.3727	0.572 12	0.4711	0.916 62	0.1579
0.313 55	0.3994	0.632 39	0.4518	0.961 66	0.0771
0.371 52	0.4364				
$xH_3CCO_2C_2H_5 + (1 - x)C_6H_{13}Cl$					
0.037 40	0.0687	0.307 32	0.4262	0.658 60	0.4955
0.055 23	0.0988	0.327 33	0.4426	0.703 64	0.4666
0.105 82	0.1812	0.405 24	0.4944	0.780 60	0.3943
0.149 28	0.2476	0.447 06	0.5116	0.860 54	0.2827
0.178 23	0.2859	0.511 29	0.5283	0.908 21	0.2010
0.237 95	0.3580	0.541 41	0.5277	0.965 23	0.0801
0.277 85	0.3985	0.599 63	0.5195		
$xH_3CCO_2C_2H_5 + (1 - x)C_7H_{15}Cl$					
0.045 80	0.0901	0.377 67	0.5130	0.703 04	0.5222
0.105 79	0.1947	0.433 03	0.5457	0.709 26	0.5167
0.156 40	0.2725	0.491 84	0.5680	0.806 29	0.4118
0.213 52	0.3499	0.531 39	0.5750	0.877 18	0.2961
0.263 11	0.4084	0.594 87	0.5727	0.938 97	0.1629
0.307 91	0.4548	0.640 57	0.5574	0.979 45	0.0578
$xH_3CCO_2C_2H_5 + (1 - x)C_8H_{17}Cl$					
0.046 78	0.0937	0.392 76	0.5538	0.704 54	0.5671
0.094 13	0.1776	0.417 99	0.5713	0.746 83	0.5285
0.146 46	0.2637	0.490 75	0.6082	0.813 65	0.4414
0.191 13	0.3353	0.515 50	0.6138	0.831 63	0.4130
0.223 67	0.3761	0.554 12	0.6191	0.864 37	0.3546
0.283 97	0.4516	0.604 70	0.6146	0.935 11	0.1934
0.313 05	0.4832	0.642 72	0.6034	0.979 91	0.0635
0.336 72	0.5062				

Experimental Results and Conclusions

The excess molar volumes, V^E_m, for the eight mixtures made up of ethyl formate or ethyl acetate with the 1-chloroalkanes (from pentane to octane), at 298.15 K, are given in Table II.

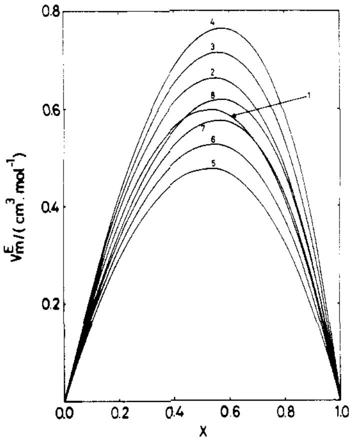

Figure 1. Excess molar volumes at 298.15 K for $\{xHCO_2C_2H_5 + (1 - x)C_nH_{2n+1}Cl\}$, n = 5 (1), n = 6 (2), n = 7 (3), n = 8 (4), and for $\{xH_3CCO_2C_2H_5 + (1 - x)C_nH_{2n+1}Cl\}$, n = 5 (5), n = 6 (6), n = 7 (7), n = 8 (8).

The experimental points of each mixture were correlated by means of a polynomial function in Z proposed by one of us (*10*) and which has given excellent results in the fitting of excess thermodynamic functions. The equation adopts the form

$$V^E_m(\text{cm}^3\cdot\text{mol}^{-1}) = x(1 - x) \sum_1 A_{i-1}Z^{i-1} \qquad (i = 1, 2, ...) \quad (1)$$

where

$$Z = x/(x + k(1 - x)) \quad (2)$$

and was defined for each of the mixtures by means of a least-squares method. The number of coefficients A_i was determined in each case by applying a F-test to the successive terms, while the parameter k was obtained by optimization in order to obtain the minimum standard deviation, $s(V^E_m)$, of the fit. All these values are listed in Table III. For this equation the value of k must always be positive, since if $k < 0$, the function Z, defined by eq 2, will present a discontinuity in $x = k/(1 + k)$. The curves of Figure 1 indicate the values calculated by using the corresponding fitting equation, it being observed that the V^E_m values of the systems studied were positive over the concentration range, x, of the ester.

The excess molar volumes increase, for any one ester, with the length of the chain the 1-chloroalkane. However, the opposite effect is produced when a certain 1-chloroalkane interacts with the esters. In this case, the V^E_m values decrease as the chain R accompanying the carboxylate group R–CO–O–C_2H_5 of the ester lengthens. This effect is similar to that occurring in the interaction of ester + n-alkane (*3*) or in that of ester + 1-alkanol (*4*). As the number of $-CH_2-$ groups in R increases, the polarity of the ester group decreases, the contacts among groups consequently weakening and permitting the accommodation of the molecules of the 1-chloroalkane among the molecules of the ester, as well as the formation of some bonds among the two types of molecules present. This explanation is also manifested through the results obtained with other thermodynamic functions, such as H^E_m, or by means of the theory of Nitta et al. (*11*) that explains their behavior as a function of the number of contacts among groups. In this type of mixtures, a decrease in the number of ester–ester contacts may exist with relation to that for pure esters, due to the inclusion of molecules of 1-chloroalkanes among the molecules of the ester. This is the reason why all these mixtures produce endothermic effects in their mixing processes. The fall in the number of ester–ester contacts increases with the length of the 1-chloroalkane chain and with the increase of $-CH_2-$ groups in R. It is also interesting to compare our the volumetric data with those obtained for the mixtures of ethyl formate and ethyl

Table III. Coefficients of Eq 1 and Standard Deviations $s(V_m^E)$

mixture	k	A_0	A_1	A_2	A_3	$s(V_m^E)/cm^3 \cdot mol^{-1}$
$x HCO_2C_2H_5$ +						
$(1 - x)C_5H_{11}Cl$	0.799	2.2129	0.3786	−0.4482	0.6091	0.0010
$(1 - x)C_6H_{13}Cl$	1.517	2.3709	0.4333	0.5574		0.0009
$(1 - x)C_7H_{15}Cl$	2.672	2.4205	1.4856			0.0010
$(1 - x)C_8H_{17}Cl$	0.876	2.3550	1.6302	−2.1599	2.5877	0.0009
$x H_3CCO_2C_2H_5$ +						
$(1 - x)C_5H_{11}Cl$	1.816	1.7902	0.3234			0.0009
$(1 - x)C_6H_{13}Cl$	0.515	1.8684	0.3698	−0.5260	0.7603	0.0009
$(1 - x)C_7H_{15}Cl$	0.956	2.0409	0.0131	0.8865		0.0006
$(1 - x)C_8H_{17}Cl$	1.325	2.0357	0.6679	0.6265		0.0011

acetate with *n*-alkanes and 1-alkanols, it being verified that at an equal number of carbon atoms, the following order is fulfilled: V_m^E(*n*-alkane) > V_m^E(1-chloroalkane) > V_m^E(1-alkanol). This sequence is coherent if the inertness of *n*-alkane is taken into account vs. the high polarity of the Cl in the alkyl chloride and, of course, the dissociation of the polymers of the 1-alkanol by way of hydrogen bonds which are generally the main cause of the nonideal behavior of associated solutions.

In order to accompany the explanation of the volumetric behavior of these mixtures, the partial molar excess volumes of the two homologous series studied here were also determined. A systematic increase in the V_i^E values was observed, for any one ester, with the lengthening of the 1-chloroalkane chain. The V_2^E values of the aliphatic chloride in the ester-rich region increase considerably in relation to those found for the mixtures of 1-chloroalkane + aliphatic hydrocarbons (*3*, *12*) and + 1-alkanols (*13*). A point noted by Pérez et al. (*13*) for 1-chlorobutane + 1-alkanol mixtures is also included here, which considers a Cl–aliphatic group interaction to be due to their influence on the free-volume effects.

However, the interpretation presented here will be checked and extended as further experimental results, which will be reported elsewhere, become available.

Glossary

A_i	parameters of eq 1
k	parameter of eq 2
n_D	refractive index at sodium D line
s	standard deviation
V_m^E	excess molar volumes, $cm^3 \cdot mol^{-1}$
x	liquid mole fraction
Z	function defined by eq 2

Greek Letters

ρ	density, $kg \cdot m^{-3}$

Registry No. $HCO_2C_2H_5$, 109-94-4; $H_3CCO_2C_2H_5$, 141-78-6; $C_5H_{11}Cl$, 543-59-9; $C_6H_{13}Cl$, 544-10-5; $C_7H_{15}Cl$, 629-06-1; $C_8H_{17}Cl$, 111-85-3.

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