J. Chem. Eng. Data **1988**, *33*, 260-262

Literature Cited

(1) Alonso, M.; Recasens, F. *J. Chem. Eng. Data* **1986**, *31*, 164.
(2) Sorensen, J. M.; Arlt, E. *DECHEMA Chemistry Data Series Liquid-Liquid Equilibrium Data Collection*; VCH: Weinheim, FRG, 1980; Vol. 5.
(3) Treybal, R. E.; Weber, L. D.; Daley, J. F. *Ind. Eng. Chem.* **1946**, *38*, 817.
(4) Ishida, K. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 693.
(5) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(6) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(7) Sorensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, A. *Fluid Phase Equilib.* **1979**, *3*, 47.

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V_m^E of Mixtures Containing Ethyl Propanoate or Ethyl Butanoate with 1-Chloroalkanes

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The excess molar volumes, V_m^E, of the binary mixtures ethyl propanoate + 1-chloroalkanes and ethyl butanoate + 1-chloroalkanes are indirectly determined from densities at 298.15 K. All the systems studied exhibit positive excess molar volumes along the range of concentrations, increasing, for a specific ester, with the 1-chloroalkane chain. On the contrary, the V_m^Es decrease with the increase in R_1 in R_1–CO–O–C_2H_5, upon mixing with a specific 1-chloroalkane.

Introduction

As a continuation of our study of the excess thermodynamic properties of binary systems formed by aliphatic esters with alkyl chlorides the V_m^Es of the mixtures $\{xC_mH_{2m+1}CO_2C_2H_5$ (m = 2, 3) + $(1 - x)ClC_nH_{2n+1}$ (n = 5, 6, 7, 8)$\}$ are presented here. In a previous article (*1*) we reported the excess molar volumes of the systems formed by the same 1-chloroalkanes with other ethyl esters (formate and acetate). In order to perform a more through analysis of the volumetric behavior of these systems, the data presented in (*1*) will be used, aiding confirmation of the considerations carried out in the interpretation of the results.

Taking into account other works reported in the same field of research we found analogies between our results and the plots of V_m^Es versus composition of mixtures of aliphatic esters and ketones with other compounds such as n-alkanes (*2*, *3*) and n-alkanols (*4*, *5*) having a similar molecular structure. These analogies are mainly manifested by two effects: The first is the increase in the V_m^Es for any one ester or ketones with the length of the chain of the second compound (n-alkane, n-alkanol, or 1-chloroalkane). The second, and more difficult to define, is the decrease in the V_m^Es of the mixture with an R_1–CO–O–R_2 ester or a R_1–CO–R_2 ketone, as the length of the aliphatic radicals, R_1 or R_2, increases if the second compound is the same one.

Dusart et al. found some anomalies in the behavior of mixtures containing certain esters and ketones by means of volumetric (*3*), spectroscopic (*6*), and enthalpic (*7*) studies, attributing them to the existence of pseudocycles brought about by turns around the bonds joined on either side to the carbonyl group, =C=O. The existence of these rotational isomers have also been observed by Mido et al. (*8*) in esters and by Hirota et al. (*9*), Shimanouchi et al. (*10*), and Redondo et al. (*11*) in ketones, among others. These and other considerations will be taken into account when justifying the behavior of some of the systems studied in this work.

Experimental Section

The characteristics of the 1-chloroalkanes used in this work were reported in a previous paper (*1*). The purity specifications indicated by the manufacturer, Fluka, were the following: for ethyl propanoate, puriss >99 mol %, and for ethyl butanoate, purum >98 mol %. However, all products were degassed in vacuo and later dried with a molecular sieve (Union Carbide, Type 4A, from Fluka). After this treatment the physical properties experimentally determined by us and those taken from data found in the literature (in parentheses) at 298.15 K are as follows: for ethyl propanoate, ρ = 883.98 kg·cm^{-3} (884.0 (*12*)) and n_D = 1.3817 (1.3814 (*12*)); for ethyl butanoate, ρ = 872.73 kg·m^{-3} (873.94 (*12*)) and n_D = 1.3896 (1.3904 (value estimated from ref *12*)).

Preparation of samples, the technique of density measurements, and determination of the excess molar volumes were as described in previous papers (*13*, *14*). The mean errors in V_m^E were smaller than ±0.0003 cm^3·mol^{-1} as indicated in (*1*).

Results and Discussion

V_m^Es of the $\{xC_mH_{2m+1}CO_2C_2H_5$ (m = 2, 3) + $(1 - x)ClC_nH_{2n+1}$ (n = 5, 6, 7, 8)$\}$ systems determined from the densities and over the entire range of concentrations are given in Table I. V_m^Es were correlated as a function of the composition of the ester by using a polynomial expression which has afforded excellent results in the treatment of excess thermodynamic magnitudes. The equation has the form

$$V_m^E\ (\mathrm{cm^3{\cdot}mol^{-1}}) = x(1 - x)\sum A_i\{x/[x + k(1 - x)]\}^i \qquad i = 0, 1, 2, \ldots \quad (1)$$

The coefficients A_i for each system were determined by using a least-squares linear regression procedure (employing an F-test). Each of the correlations was optimized for the best

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Table I. Excess Molar Volumes, V_m^E, at 298.15 K for Ester (1) + 1-Chloroalkanes (2) Mixtures

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	$V_m^E/cm^3 \cdot mol^{-1}$
Ethyl Propanoate + 1-Chloropentane							
0.014 88	0.0151	0.232 32	0.2075	0.490 62	0.2944	0.785 80	0.1975
0.043 94	0.0474	0.286 81	0.2386	0.538 40	0.2929	0.882 60	0.1231
0.097 78	0.1012	0.352 04	0.2676	0.570 02	0.2876	0.907 13	0.1002
0.130 16	0.1310	0.404 52	0.2822	0.647 20	0.2695	0.940 92	0.0658
0.199 74	0.1856	0.441 61	0.2895	0.728 98	0.2326	0.969 92	0.0332
Ethyl Propanoate + 1-Chlorohexane							
0.032 18	0.0406	0.328 91	0.2925	0.547 04	0.3391	0.899 29	0.1290
0.064 66	0.0786	0.392 35	0.3184	0.598 96	0.3319	0.931 96	0.0901
0.109 83	0.1283	0.414 62	0.3256	0.654 31	0.3145	0.972 73	0.0367
0.162 32	0.1763	0.437 58	0.3310	0.725 01	0.2796		
0.209 59	0.2158	0.462 90	0.3357	0.756 95	0.2597		
0.263 91	0.2551	0.491 90	0.3388	0.828 20	0.2027		
Ethyl Propanoate + 1-Chloroheptane							
0.037 20	0.0535	0.328 63	0.3178	0.562 00	0.3799	0.855 85	0.2080
0.11090	0.1384	0.397 10	0.3517	0.620 38	0.3691	0.939 13	0.0980
0.158 89	0.1872	0.444 67	0.36720	0.678 80	0.3481	0.947 66	0.0856
0.218 08	0.2396	0.495 27	0.3789	0.727 96	0.3216		
0.258 88	0.2911	0.544 91	0.3808	0.780 70	0.2827		
Ethyl Propanoate + 1-Chlorooctane							
0.043 84	0.0644	0.272 32	0.3084	0.560 51	0.4204	0.767 28	0.3280
0.083 67	0.1148	0.353 41	0.3648	0.588 18	0.4185	0.846 22	0.2460
0.140 58	0.1830	0.394 11	0.3262	0.641 51	0.4040	0.933 36	0.1189
0.167 13	0.2115	0.476 09	0.4137	0.659 09	0.3979	0.976 92	0.0441
0.223 04	0.2667	0.511 41	0.4208	0.718 71	0.3667		
Ethyl Butanoate + 1-Chloropentane							
0.014 07	0.0149	0.240 01	0.1590	0.647 50	0.1859	0.869 94	0.0922
0.026 91	0.0278	0.304 58	0.1837	0.661 78	0.1822	0.922 45	0.0548
0.054 34	0.0499	0.349 99	0.1944	0.676 69	0.1782	0.937 75	0.0430
0.0.4 54	0.0799	0.478 73	0.2108	0.727 73	0.1610	0.967 41	0.0216
0.128 30	0.1015	0.518 27	0.2100	0.785 56	0.1356	0.983 12	0.0096
0.183 70	0.1344	0.582 82	0.1993	0.846 29	0.1071		
Ethyl Butanoate + 1-Chlorohexane							
0.032 23	0.0360	0.274 26	0.1999	0.564 81	0.2504	0.904 98	0.0889
0.077 99	0.0768	0.329 67	0.2230	0.622 18	0.2387	0.955 30	0.0429
0.119 62	0.1095	0.392 43	0.2406	0.698 74	0.2142	0.970 22	0.0278
0.154 11	0.1341	0.463 56	0.2529	0.781 03	0.1751		
0.212 12	0.1697	0.531 49	0.2543	0.845 44	0.1339		
Ethyl Butanoate + 1-Chloroheptane							
0.035 68	0.0372	0.312 59	0.2338	0.611 38	0.2710	0.884 74	0.1225
0.101 50	0.0982	0.352 63	0.2493	0.679 22	0.2523	0.933 01	0.0768
0.142 91	0.1299	0.439 48	0.2731	0.740 37	0.2242	0.972 76	0.0320
0.202 99	0.1732	0.504 25	0.2799	0.823 82	0.1732		
0.260 55	0.2074	0.540 02	0.2796	0.848 43	0.1534		
Ethyl Butanoate + 1-Chlorooctane							
0.039 14	0.0464	0.266 18	0.2429	0.538 37	0.3257	0.879 26	0.1510
0.094 20	0.1044	0.328 35	0.2751	0.598 57	0.3199	0.936 19	0.0868
0.142 34	0.1483	0.371 84	0.2949	0.649 90	0.3061	0.974 10	0.0351
0.173 54	0.1751	0.448 89	0.3163	0.728 08	0.2728		
0.216 10	0.2072	0.508 90	0.3243	0.809 89	0.2153		

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

mixture	K	A_0	A_1	A_2	A_3	$s(V_m^E)/cm^3 \cdot mol^{-1}$
ethyl propanoate +						
1-chloropentane	0.030	1.0119	0.1610	0.0002		0.0007
1-chlorohexane	0.316	1.3374	−0.2263	0.3354		0.0006
1-chloroheptane	0.388	1.4968	−0.5434	0.7879		0.0007
1-chlorooctane	0.546	1.5177	−0.1527	0.6116		0.0008
ethyl butanoate +						
1-chloropentane	0.203	1.1405	−0.9835	1.3341	−0.7089	0.0018
1-chlorohexane	0.109	1.3032	−0.7313	0.4562		0.0009
1-chloroheptane	0.598	1.0716	−0.0631	0.2208		0.0006
1-chlorooctane	0.534	1.2350	−0.1539	0.3832		0.0008

value of the parameter k, by minimization of standard deviation, $s(V_m^E)$, of the experimental data with regard to those estimated by means of eq 1. The numerical values of the parameters of eq 1, as well as the $s(V_m^E)$s corresponding to each system, are presented in Table II. The plots of the V_m^Es, all of which are positive, are given in Figure 1 for all the systems studied.

Two important quantitative aspects can be observed in Figure 1. The first is that for any one ester the V_m^Es of the mixtures increase with the number of $-CH_2-$ groups of the 1-chloroalkane chain, while a shift occurs in the maxima of the curves toward more ester-enriched concentrations. This behavior, the size effect, is also present in the mixtures ester + n-alkanes

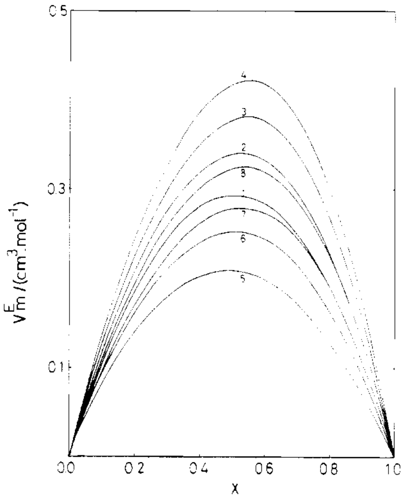

Figure 1. V_m^E for the following binary systems: $C_3H_7CO_2C_2H_5$ + $C_nH_{2n+1}Cl$ (n = 5 (1), n = 6 (2), n = 7 (3), n = 8 (4)) and $C_4H_9CO_2C_2H_5$ + $C_nH_{2n+1}Cl$ (n = 5 (5), n = 6 (6), n = 7 (7), n = 8 (8)).

(*2*) and ester + n-alkanols (*4*, *5*) and, in our case, is explained by the fact that, as the length of the ClC_nH_{2n+1} increases, the steric hindrance also increases, thus impeding the dipole–dipole interaction between the -CO-O- and >C-Cl polar groups. If the values obtained in this work are combined with those reported in ref *1* and then the V_m^Es for x = 0.5 are estimated, it is found that the above-mentioned increase occurs lineally, for all the esters, with the number of carbon atoms, n, of the 1-chloroalkane.

The second aspect is that, for a specific 1-chloroalkane, the V_m^Es decrease with the increase in length of the aliphatic radical R_1 bonded to the carbonyl group of the ester, R_1-CO-O-C_2H_5. This behavior is also observed in mixtures of aliphatic esters with n-alkanes (*3*) and with n-alkanols (*4*), as well as in mixtures of aliphatic ketones + n-alkanes (*3*), even when one of the alkyl radicals of the ketone or of the ester is substituted by a phenol group (*3*). The partial molar volume curves were also determined from the data obtained in this and the previous work (*1*), by way of eq 1. A systematic increase of the $V_{m,i}^{E\infty}$s is observed with the increase in the 1-chloroalkane chain. Particularly, the values at infinite dilution calculated by means of

$$V_{m,2}^{E\infty} = \sum A_i \qquad (2)$$

are plotted in Figure 2 for the four chloroalkanes in the different ethyl esters, $C_mH_{2m+1}CO_2C_2H_5$ (m = 0, 1, 2, 3), versus the number of carbon atoms, m, of the aliphatic radical $C_mH_{2m+1}^-$. The same distribution is obtained taking V_m^Es at x = 0.5. The specific behavior of mixtures with ethyl formate can be explained by means of the spectroscopic study carried out by Wilmhurst (*17*) who draws attention to the anomaly presented by formates with respect to the other esters in forming strong intermolecular associations by means of hydrogen bonds, without precluding the formation of dimers. The hydrogen-bond associations are much stronger than dipole–dipole associations between ester molecules, which explains the greatest values of V_m^E. The sequence observed in the V_m^Es for mixtures with ethyl acetate, ethyl propanoate, and ethyl butanoate can be explained by taking into account that the basic nature of the carbonyl group increases as the chain of the ethyl ester lengthens (*18*), the ester–ester interactions therefore weakening and permitting a greater contact between the 1-chloroalkane and the ester. This effect makes the positive contributions to the V_m^Es of the mixture progressively smaller.

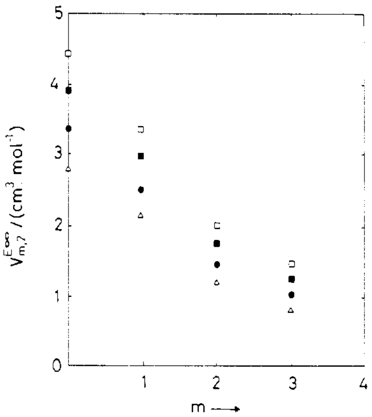

Figure 2. Excess molar volumes at infinite dilution for $C_nH_{2n+1}Cl$, n = 5 (△); n = 6 (●); n = 7 (■), and n = 8 (□), in $C_mH_{2m+1}CO_2C_2H_5$ (m = 0, 1, 2, 3) as a function of m.

The IR spectra obtained by us show a widening of the carbonyl band of ethyl butanoate, which is due to the existence of rotational isomers (*19*), a pseudocycle being formed as proposed by Dusart et al. (*3*). This fact causes V_m^E values to be greater than expected.

Registry No. $C_2H_5CO_2C_2H_5$, 105-37-3; $C_3H_7CO_2C_2H_5$, 105-54-4; 1-chloropentane, 543-59-9; 1-chlorohexane, 544-10-5; 1-chloroheptane, 629-06-1; 1-chlorooctane, 111-85-3.

Literature Cited

(1) Ortega, J.; Matos, J. S.; Paz-Andrade, M. I.; Fernández, J. *J. Chem. Eng. Data* **1987**, *32*, 464.
(2) Grolier, J.-P. E.; Ballet, O.; Viallard, A. *J. Chem. Thermodyn.* **1974**, *6*, 895.
(3) Dusart, O.; Piekarski, C.; Piekarski, S.; Viallard, A. *J. Chim. Phys.* **1976**, *73*, 837.
(4) Fernández, J.; Berro, Ch.; Peneloux, A. *J. Chem. Eng. Data* **1987**, *32*, 17.
(5) Ortega, J.; Paz-Andrade, M. I.; Rodriguez-Nuñez, E.; Romani, L. *Aust. J. Chem.* **1985**, *38*, 1435.
(6) Dusart, O.; Piekarski, C.; Piekarski, S. *J. Chim. Phys.* **1976**, *73*, 832.
(7) Dusart, O.; Piekarski, S.; Grolier, J-P.E. *J. Chim. Phys.* **1979**, *76*, 433.
(8) Mido, L.; Kawasmita, T.; Susuki, K. *J. Mol. Struct.*, in press.
(9) Hirota, M.; Hagiwara, T.; Satonaka, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2439.
(10) Shimanouchi, T.; Abe, L.; Mikami, M. *Spectrochim. Acta* **1968**, *24*, 1037.
(11) Redondo, M. I.; Garcia, M. V.; Notario, R.; Morcillo, J. *J. Mol. Struct.* **1986**, *142*, 239.
(12) Riddick, J. H.; Bunger, W. B.; Sakano, T. K. *Organic Solvent*, 3rd ed.; Wiley-Interscience: New York, 1986.
(13) Ortega, J.; Matos, J. S.; Paz-Andrade, M. I.; Jimenez, E. *J. Chem. Thermodyn.* **1985**, *17*, 1127.
(14) Ortega, J.; Matos, J. S. *Mater. Chem. Phys.* **1986**, *15*, 415.
(15) Navarro, J. M.; Baloira, M.; Bravo, R.; Paz-Andrade, M. I.; Sarmiento, F. *J. Chem. Thermodyn.* **1985**, *17*, 447.
(16) Fernandez, J.; Paz-Andrade, M. I.; Sarmiento, F.; Bravo, R. *J. Chem. Thermodyn.* **1983**, *15*, 1145.
(17) Wilmhurst, J. K. *J. Mol. Spectrosc.* **1957**, *1*, 201.
(18) Navarro, R.; Gallego, E.; Morcillo, J. *Anal. Quim. España* **1982**, *78*, 326.
(19) George, W. O.; Hassid, D. V.; Maddams, W. S. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1030.

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