Excess Molar Volumes of Ethylbenzene and (2-Chloroethyl)benzene + Five Methyl *n*-Alkyl Ketones at 298.15 K

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Excess molar volumes V_m^E of ethylbenzene and (2-chloroethyl)benzene + five methyl *n*-alkyl ketones have been determined from density measurements at 298.15 K and atmospheric pressure by means of an Anton Paar digital density meter. Values of V_m^E are negative for all mixtures with the exception of the (2-chloroethyl)-benzene + 2-undecanone system which presents an inversion of sign. The variation of V_m^E with molecular size is discussed.

Introduction

Recently, we have focused our research program on a study of the thermodynamic properties of methyl *n*-alkyl ketones, and our previous publications (*1-3*) report either excess molar enthalpies or excess molar volumes of binary mixtures containing these ketones. As a continuation of these studies, this paper reports the dependence of excess molar volumes V_m^E on composition for binary systems containing ethyl-benzene or (2-chloroethyl)benzene + five methyl *n*-alkyl ketones (2-propanone, 2-butanone, 2-pentanone, 2-octanone, or 2-undecanone).

In a previous paper (*4*) we reported the excess molar enthalpies H_m^E for the same binary mixtures, and the aim of this study was to provide more information about the thermodynamic properties of these mixtures.

We are not aware of any excess volume measurements in the literature for the systems studied, with the exception of ethylbenzene + 2-propanone or + 2-butanone which were studied by Quin et al. (*5*) but at 293.15 K.

Materials and Density Measurements

Ethylbenzene and (2-chloroethyl)benzene (component 1), obtained from Aldrich Chemical Co., with a grade of purity higher than 99% were used as supplied. Methyl *n*-alkyl ketones, also obtained from Aldrich, with the exception of 2-pentanone which was from Fluka, were purified as described in ref 3.

The purity of all solvents was ascertained by comparing their densities ρ with the corresponding literature values; see Table I. Densities ρ were determined by means of a digital density meter (Anton Paar DMA 60) equipped with a density-measuring cell (DMA 602), with a sensitivity to 10^{-6} g cm^{-3}.

The temperature was maintained constant to less than ±0.005 K by means of a Heto thermostat bath type 01 DBT 623. The temperature of the measuring cell was measured with a digital thermometer (Anton Paar DT 100-25) inserted into the jacket of the measuring cell.

The density meter was calibrated with water and dry air,

Table I. Densities ρ of Pure Solvents at 298.15 K

component	ρ/(g cm^{-3}) this paper	lit.
ethylbenzene	0.862 65	0.862 53 (*7*)
(2-chloroethyl)benzene	1.068 51	1.069 (*8*)
2-propanone	0.785 01	0.784 40 (*7*)
2-butanone	0.799 91	0.799 7 (*7*)
2-pentanone	0.801 40	0.801 5 (*7*)
2-octanone	0.814 86	0.814 3 (*7*)
2-undecanone	0.821 70	no lit. data at 298.15 K

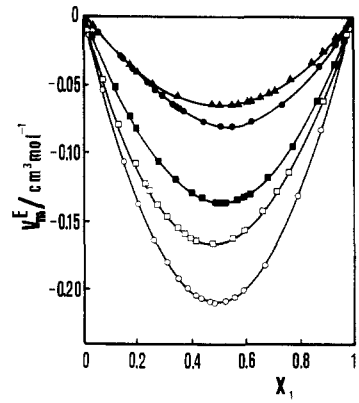

Figure 1. Excess molar volumes at 298.15 K for the binary mixtures of ethylbenzene + 2-propanone (●), + 2-butanone (□), + 2-pentanone (○), + 2-octanone (■), and + 2-undecanone (▲).

and experiments were done at 298.15 K and at atmospheric pressure.

The test system benzene + cyclohexane was used to evaluate the accuracy of the experimental technique, and the results obtained are in agreement with those of the literature (*6*) (the accuracy in the volume at about equimolar composition is less than 0.002 cm^3 mol^{-1}).

Mixtures were prepared from the degassed samples by weighing them into 25-mL air-tight stoppered flasks with an accuracy of 0.0001 in mole fraction, and all weights were corrected to account for the partial evaporation of the liquid. The procedure used for the preparation of the samples is similar to that described in ref 9.

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Table II. Experimental Densities ρ and Excess Molar Volumes V_m^E for Binary Mixtures of Ethylbenzene and (2-Chloroethyl)benzene + Methyl *n*-Alkyl Ketones at 298.15 K

x_1	ρ/(g cm^{-3})	V_m^E/(cm^3 mol^{-1})	x_1	ρ/(g cm^{-3})	V_m^E/(cm^3 mol^{-1})	x_1	ρ/(g cm^{-3})	V_m^E/(cm^3 mol^{-1})	x_1	ρ/(g cm^{-3})	V_m^E/(cm^3 mol^{-1})
Ethylbenzene (1) + 2-Propanone (2)											
0.0102	0.786 40	−0.0218	0.2371	0.811 96	−0.0477	0.3540	0.822 68	−0.0684	0.6200	0.842 88	−0.0769
0.0550	0.792 03	−0.0112	0.2615	0.814 31	−0.0517	0.3633	0.823 46	−0.0690	0.7337	0.849 25	−0.0644
0.1440	0.802 32	−0.0289	0.2924	0.817 21	−0.0581	0.4442	0.830 02	−0.0776	0.8685	0.856 44	−0.0359
0.1441	0.802 33	−0.0292	0.3307	0.820 66	−0.0648	0.5052	0.834 57	−0.0796	0.9327	0.859 56	−0.0200
0.1865	0.806 86	−0.0378	0.3410	0.821 56	−0.0665	0.5452	0.837 40	−0.0800	0.9718	0.861 37	−0.0069
Ethylbenzene (1) + 2-Butanone											
0.0148	0.801 03	−0.0106	0.2454	0.820 12	−0.1304	0.3992	0.830 92	−0.1616	0.6641	0.846 70	−0.1435
0.0695	0.805 91	−0.0466	0.2758	0.822 36	−0.1391	0.4166	0.832 08	−0.1654	0.7166	0.849 47	−0.1293
0.1282	0.810 89	−0.0799	0.3131	0.825 02	−0.1465	0.4788	0.836 02	−0.1672	0.7608	0.851 70	−0.1146
0.1901	0.815 87	−0.1077	0.3509	0.827 67	−0.1550	0.5516	0.840 41	−0.1635	0.8869	0.857 71	−0.0615
0.2284	0.818 82	−0.1222	0.3768	0.829 43	−0.1598	0.5944	0.842 87	−0.1579	0.9725	0.861 48	−0.0161
Ethylbenzene (1) + 2-Pentanone (2)											
0.0165	0.802 71	−0.0133	0.3070	0.823 37	−0.1801	0.4802	0.834 44	−0.2100	0.6664	0.845 35	−0.1832
0.0687	0.806 63	−0.0545	0.3488	0.826 13	−0.1926	0.4808	0.834 48	−0.2108	0.7933	0.852 24	−0.1313
0.1466	0.812 31	−0.1077	0.3836	0.828 37	−0.1992	0.5250	0.837 15	−0.2090	0.8806	0.856 76	−0.0829
0.2030	0.816 30	−0.1386	0.4169	0.830 50	−0.2053	0.5557	0.838 98	−0.2064	0.9795	0.861 67	−0.0154
0.2614	0.820 31	−0.1647	0.4319	0.831 44	−0.2065	0.5873	0.840 83	−0.2013			
Ethylbenzene (1) + 2-Octanone (2)											
0.0313	0.866 03	−0.0159	0.3337	0.828 93	−0.1201	0.5252	0.837 80	−0.1369	0.7694	0.850 02	−0.0974
0.1164	0.819 53	−0.0535	0.3978	0.831 83	−0.1292	0.5666	0.839 80	−0.1353	0.7694	0.850 02	−0.0974
0.1702	0.821 79	−0.0742	0.4359	0.833 60	−0.1358	0.5958	0.841 22	−0.1318	0.9318	0.858 78	−0.0336
0.1935	0.822 78	−0.0814	0.4927	0.836 26	−0.1374	0.6105	0.841 94	−0.1297	0.9804	0.861 52	−0.0094
0.2774	0.826 43	−0.1080	0.5046	0.836 83	−0.1378	0.6788	0.845 34	−0.1195			
Ethylbenzene (1) + 2-Undecanone (2)											
0.0308	0.823 93	−0.0070	0.4686	0.837 09	−0.0663	0.6184	0.842 88	−0.0605	0.8469	0.853 66	−0.0325
0.1665	0.827 51	−0.0350	0.5019	0.838 30	−0.0657	0.6515	0.844 29	−0.0592	0.8878	0.855 91	−0.0257
0.1969	0.828 37	−0.0409	0.5502	0.840 14	−0.0644	0.6860	0.845 80	−0.0555	0.9396	0.858 89	−0.0128
0.2624	0.830 29	−0.0501	0.5731	0.841 04	−0.0630	0.7064	0.846 73	−0.0541	0.9870	0.861 83	−0.0034
0.3443	0.832 85	−0.0594	0.6099	0.842 53	−0.0615	0.7662	0.849 55	−0.0468			
(2-Chloroethyl)benzene (1) + 2-Propanone (2)											
0.0128	0.791 75	−0.0340	0.1906	0.872 04	−0.3598	0.3534	0.928 68	−0.4669	0.6448	1.003 61	−0.3611
0.0508	0.810 88	−0.1257	0.2246	0.885 05	−0.3985	0.3837	0.937 89	−0.4729	0.7393	1.022 76	−0.2738
0.0978	0.832 98	−0.2220	0.2809	0.905 11	−0.4389	0.4270	0.950 34	−0.4688	0.8063	1.035 23	−0.2079
0.1218	0.843 62	−0.2644	0.3169	0.917 12	−0.4550	0.4456	0.955 47	−0.4662	0.9688	1.062 22	−0.0337
0.1446	0.853 37	−0.2996	0.3373	0.923 65	−0.4611	0.5450	0.980 97	−0.4298			
(2-Chloroethyl)benzene (1) + 2-Butanone (2)											
0.0126	0.804 85	−0.0306	0.2635	0.895 17	−0.4188	0.4322	0.944 58	−0.4747	0.6885	1.006 72	−0.3487
0.0878	0.834 35	−0.1899	0.3302	0.915 61	−0.4552	0.4645	0.953 21	−0.4725	0.7734	1.024 56	−0.2672
0.1059	0.841 10	−0.2229	0.3525	0.922 20	−0.4664	0.5016	0.962 81	−0.4639	0.8550	1.040 63	−0.1777
0.1646	0.862 22	−0.3129	0.3712	0.927 60	−0.4691	0.5300	0.969 92	−0.4522	0.9744	1.062 48	−0.0318
0.2177	0.880 33	−0.3792	0.4057	0.937 84	−0.4754	0.5825	0.982 67	−0.4259			
(2-Chloroethyl)benzene (1) + 2-Pentanone (2)											
0.0164	0.807 05	−0.0357	0.3312	0.905 11	−0.4284	0.5061	0.952 84	−0.4456	0.7821	1.019 93	−0.2655
0.0829	0.829 18	−0.1636	0.3515	0.910 88	−0.4359	0.5328	0.959 74	−0.4389	0.8227	1.029 05	−0.2219
0.1525	0.851 52	−0.2697	0.4374	0.934 61	−0.4536	0.5520	0.964 66	−0.4326	0.8665	1.038 69	−0.1723
0.2576	0.883 68	−0.3821	0.4463	0.937 00	−0.4519	0.6190	0.981 39	−0.3970	0.9801	1.062 82	−0.0270
0.2872	0.892 40	−0.4047	0.4657	0.942 20	−0.4507	0.7341	1.008 89	−0.3107			
(2-Chloroethyl)benzene (1) + 2-Octanone (2)											
0.0235	0.819 92	−0.018 73	0.4261	0.912 69	−0.189 7	0.5953	0.955 23	−0.1826	0.8178	1.014 78	−0.1095
0.1245	0.842 16	−0.088 61	0.4626	0.921 69	−0.191 7	0.6228	0.962 64	−0.1766	0.890 66	1.035 25	−0.0690
0.2617	0.873 45	−0.155 75	0.4830	0.926 73	−0.191 5	0.6773	0.976 67	−0.1620	0.9185	1.043 20	−0.0511
0.3236	0.887 99	−0.172 86	0.5129	0.934 21	−0.190 8	0.7150	0.986 72	−0.1493	0.9889	1.063 68	−0.0076
0.3767	0.900 70	−0.183 9	0.5431	0.941 85	−0.188 5	0.7345	0.991 97	−0.1432			
(2-Chloroethyl)benzene (1) + 2-Undecanone (2)											
0.0298	0.827 85	−0.0015	0.4337	0.903 06	0.0075	0.6616	0.958 26	−0.0175	0.8339	1.008 75	−0.0162
0.0852	0.836 84	−0.0030	0.5149	0.921 45	0.0116	0.6946	0.967 28	−0.0182	0.9237	1.038 88	−0.0100
0.1380	0.845 75	−0.0031	0.5607	0.932 42	0.0146	0.7286	0.976 88	−0.0190	0.9418	1.045 35	−0.0068
0.2314	0.862 40	−0.0018	0.6091	0.944 51	0.0166	0.7676	0.988 28	−0.0207	0.9825	1.060 30	−0.0025
0.3700	0.889 52	0.0033	0.6356	0.951 37	0.0171	0.7821	0.992 64	−0.0186			

Results and Discussion

The experimental data are given in Table II. A Redlich–Kister polynomial was used to fit the volumetric data, as

$$V_m^E/(\text{cm}^3\ \text{mol}^{-1}) = x_1 x_2 \sum_{k\geq 0} a_k (x_1 - x_2)^k \qquad (1)$$

where x_1 and x_2 denote the mole fractions of components 1 and 2. The parameters a_k of eq 1 are given in Table III with the values of the standard deviations of excess volumes $\sigma(V_m^E)$ defined as

$$\sigma(V_m^E) = \left\{ \sum_{k=1}^{N} \left[\frac{(V_m^E(\text{calcd}) - V_m^E)^2}{N - n} \right] \right\}^{0.5} \qquad (2)$$

Table III. Parameters a_k of Equation 1 and Standard Deviations $\sigma(V_m^E)$ for the Representation of Excess Volumes of Ethylbenzene or (2-Chloroethyl)benzene + Methyl *n*-Alkyl Ketones

system	a_0	a_1	a_2	$\sigma(V_m^E)$/ (cm^3 mol^{-1})
ethylbenzene (1)				
+ 2-propanone (2)	−0.3199	−0.0567	0.0874	0.0006
+ 2-butanone (2)	−0.6650	0.0620		0.0008
+ 2-pentanone (2)	−0.8390	0.0403	0.0297	0.0006
+ 2-octanone (2)	−0.5490	−0.0117	0.0400	0.0007
+ 2-undecanone (2)	−0.2603	0.0020		0.0008
(2-chloroethyl)benzene (1)				
+ 2-propanone (2)	−1.7991	0.8161	−0.0849	0.0013
+ 2-butanone (2)	−1.8536	0.6168	−0.0324	0.0010
+ 2-pentanone (2)	−1.7899	0.4206		0.0010
+ 2-octanone (2)	−0.7666	0.0691		0.0008
+ 2-undecanone (2)	0.0462	0.1077		0.0007

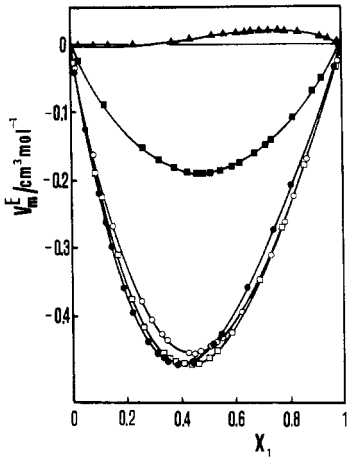

Figure 2. Excess molar volumes at 298.15 K for the binary mixtures of (2-chloroethyl)benzene + 2-propanone (●), + 2-butanone (□), + 2-pentanone (○), + 2-octanone (■), and + 2-undecanone (▲).

where V_m^E(calcd) has been determined from the right-hand side of eq 1.

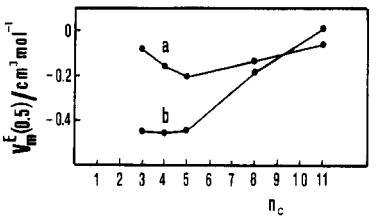

Figure 3. Values of equimolar volumes $V_m^E(0.5)$ at 298.15 K as a function of n_c for the binary mixtures of methyl *n*-alkyl ketones + ethylbenzene (a) or (2-chloroethyl)benzene (b).

The curves in Figures 1 and 2 show that the excess volumes are negative for all mixtures with the exception of (2-chloroethyl)benzene + 2-undecanone which shows an invesion of sign for $x = 0.27$. However, the magnitude of V_m^E for this mixture is small over the whole range.

Figure 3 shows $V_m^E(0.5)$, the equimolar volume of V_m^E, plotted against the number n_C of carbon atoms of methyl *n*-alkyl ketones. Mixtures of ketones with ethylbenzene show values of $V_m^E(0.5)$ decreasing with increasing n_C for $n_C \leq 5$ and then increasing slowly for $n_C \geq 5$. Similar behavior is observed when the $H_m^E(0.5)$ is plotted against n_C (*4*).

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