Articles

Excess Volumes of Cyclohexane with 2-Propanone, 2-Butanone, 3-Pentanone, 4-Methyl-2-pentanone, 1-Propanol, and 2-Propanol and Ethanoic Acid + 1-Propanol Systems

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Excess molar volumes of seven binary mixtures of cyclohexane + 2-propanone, cyclohexane + 2-butanone, cyclohexane + 3-pentanone, cyclohexane + 4-methyl-2-pentanone, cyclohexane + 1-propanol, cyclohexane + 2-propanol, and ethanoic acid + 1-propanol were derived from density measurements and correlated by Redlich−Kister equation.

Introduction

The excess molar volume of a mixture is an important thermodynamic property. In this study the excess volumes of cyclohexane + 2-propanone, cyclohexane + 2-butanone, cyclohexane + 3-pentanone, cyclohexane + 4-methyl-2-pentanone, cyclohexane + 1-propanol, cyclohexane + 2-propanol, and ethanoic acid + 1-propanol are obtained from density measurements at the temperatures of 298.15 K and 303.15 K over the entire range of concentration. Puri et al. (1974) and Radojkovic et al. (1977) have published results for cyclohexane + 2-propanone at the temperature 298.15 K, while Janssens and Ruel (1972) have measured cyclohexane + 1-propanol at 298.15 K. The results were plotted and correlated with the Redlich−Kister equation.

Experimental Section

Cyclohexane (GR grade, +99.5%) was purchased from Aldrich, 2-propanone (GR grade, +99.8%), 2-butanone (GR grade, +99.5%), 3-pentanone (GR grade, +99.0%), 4-methyl-2-pentanone (GR grade, +99.0%), 1-propanol (GR grade, +99.8%), 2-propanol (GR grade, +99.8%), and ethanoic acid (GR grade, +99.8%) were purchased from Riedel-deHaen. The deionized water (electric resistance, 18.2 MΩ·cm^{-1}) was generated by a Millipore distilled water generator. All the chemicals were verified for purity by GC analysis and carefully dried with Riedel-deHaen Type 4A molecule sieve and were used directly without further purification.

Density was measured with 25 cm^3 pycnometers (Blaubrand, Gay-Lussac type). The internal volumes of pycnometers were calibrated with pure water at the experimental temperatures. Since the room temperature was always higher than 298.15 K (one of experimental temperature), two thermostats were used. One thermostat (Neslab, RTE-221) with operating temperature range 218 K-423 K was used for the lower temperature experiments, and another thermostat (Tamson, TV-2000) was used for the higher temperature experiments. Both thermostats were controlled within the accuracy of ±0.01 K. The temperatures were measured with a platinum-resistance thermometer (Hart Scientific, 5614) calibrated with an IPTS-68. The accuracy of temperature measurement is within ±0.01 K.

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Table 1. Densities of Pure Solvents at 298.15 K and 303.15 K

		ρ/g·cm^{-3}		
solvent	T/K	experimental	literature	source
cyclohexane	298.15	0.773 85	0.773 86, 0.773 87	*a*, *f*
	303.15	0.769 14	0.768 45, 0.769 18	*b*, *f*
2-propanone	298.15	0.784 55	0.784 40	*b*
	303.15	0.778 76	0.780 33	*b*
2-butanone	298.15	0.799 92	0.799 93	*c*
	303.15	0.794 64	0.794 60	*b*
3-pentanone	298.15	0.809 77	0.809 45, 0.809 45	*b*, *f*
	303.15	0.804 86		
4-methyl-2-pentaneone	298.15	0.796 49	0.796 30, 0.796 10	*b*
	303.15	0.791 91		
1-propanol	298.15	0.799 67	0.799 62, 0.799 75	*d*, *f*
	303.15	0.795 67	0.795 70	*f*
2-propanol	298.15	0.780 86	0.780 92, 0.781 26	*e*, *f*
	303.15	0.776 61	0.777 00	*f*
ethanoic acid	298.15	1.044 62	1.043 92, 1.043 91	*b*, *f*
	303.15	1.038 95	1.038 25	*f*

[a] Radojkovic et al. (1977). [b] Riddick et al. (1986). [c] Fermeglia et al. (1988). [d] Singh et al. (1994). [e] Puri et al. (1974). [f] TRC Thermodynamic Tables.

All mixtures were prepared by directly weighing the constituent components to give a mole fraction accuracy within ±10^{-4}. In order to minimize the errors attributed to evaporation of chemicals, the denser component was charged first in preparing the solutions. Buoyancy corrections were made in this study for density measurement with pycnomerter.

For each experimental run, the pycnometer was immersed in the thermostat for 30 min to ensure temperature equilibrium. Three consecutive measurements were performed and averaged. The density was measured within accuracy of ±10^{-4} g·cm^{-3}.

Results and Discussion

Before the experiments on mixtures were conducted, the densities of pure compounds were measured and compared to the literature values to ensure the reliability of our experimental procedure. The results are given in Table 1. The present experimental values agree to literature values and data from TRC Thermodynamic Tables with the average absolute differences (AAD) of 3.44 × 10^{-4} and 3.06 × 10^{-4} g·cm^{-3}, respectively.

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Table 2. Densities and Excess Molar Volumes of Mixtures

x_1	ρ/g·cm^{-3}	V^E_{exp}/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V^E_{exp}/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V^E_{exp}/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V^E_{exp}/cm^3·mol^{-1}
Cyclohexane (1) + 2-Propanone (2)											
T = 298.15 K											
0.0801	0.779 68	0.3017	0.4588	0.768 35	1.0855	0.2543	0.772 14	0.8258	0.6985	0.768 13	0.9766
0.1356	0.776 65	0.5085	0.5366	0.767 99	1.0831	0.3186	0.770 44	0.9504	0.7937	0.769 05	0.8036
0.1954	0.774 07	0.6891	0.6204	0.767 88	1.0508	0.3886	0.769 11	1.0438	0.8922	0.770 83	0.5027
T = 303.15 K											
0.0801	0.773 52	0.3510	0.4588	0.762 74	1.1518	0.2543	0.766 18	0.8953	0.6985	0.762 92	1.0263
0.1356	0.770 42	0.5769	0.5366	0.762 46	1.1518	0.3186	0.764 58	1.0202	0.7937	0.764 00	0.8408
0.1954	0.768 02	0.7548	0.6204	0.762 55	1.1056	0.3886	0.763 40	1.1113	0.8922	0.765 94	0.5235
Cyclohexane (1) + 2-Butanone (2)											
T = 298.15 K											
0.0939	0.794 53	0.2883	0.5089	0.778 36	0.9055	0.2938	0.785 35	0.7131	0.7785	0.773 67	0.6972
0.1575	0.791 34	0.4448	0.5840	0.776 62	0.8985	0.3582	0.782 93	0.8037	0.8622	0.773 13	0.5178
0.2228	0.788 28	0.5909	0.6846	0.774 80	0.8305	0.4349	0.780 40	0.8772	0.9346	0.773 06	0.3087
T = 303.15 K											
0.0939	0.789 31	0.2927	0.5089	0.773 33	0.9263	0.2938	0.780 18	0.7323	0.7785	0.768 75	0.7201
0.1575	0.786 16	0.4515	0.5840	0.771 65	0.9168	0.3582	0.777 80	0.8245	0.8622	0.768 25	0.5388
0.2228	0.783 13	0.6010	0.6846	0.769 83	0.8552	0.4349	0.775 29	0.9023	0.9346	0.768 23	0.3252
Cyclohexane (1) + 3-Pentanone (2)											
T = 298.15 K											
0.8846	0.774 97	0.4123	0.4370	0.788 55	0.7253	0.6613	0.780 42	0.7495	0.2173	0.798 34	0.4664
0.8080	0.776 49	0.5770	0.3655	0.791 56	0.6636	0.5898	0.782 75	0.7775	0.1459	0.801 95	0.3301
0.7353	0.778 23	0.6906	0.2930	0.794 82	0.5731	0.5115	0.785 63	0.7619	0.0684	0.805 95	0.1730
T = 303.15 K											
0.8846	0.770 19	0.4243	0.4370	0.783 69	0.7403	0.6613	0.775 59	0.7666	0.2173	0.793 47	0.4738
0.8080	0.771 68	0.5931	0.3655	0.786 71	0.6731	0.5898	0.777 93	0.7903	0.1459	0.797 05	0.3362
0.7353	0.773 46	0.7002	0.2930	0.789 98	0.5796	0.5115	0.780 75	0.7822	0.0684	0.800 97	0.1863
Cyclohexane (1) + 4-Methyl-2-pentanonee (2)											
T = 298.15 K											
0.9008	0.773 88	0.3608	0.4810	0.781 61	0.7228	0.7004	0.776 60	0.6952	0.2488	0.788 26	0.4909
0.8329	0.774 56	0.5123	0.4038	0.783 69	0.6731	0.6285	0.778 00	0.7460	0.1668	0.790 94	0.3427
0.7698	0.775 36	0.6255	0.3273	0.785 92	0.5914	0.5546	0.779 71	0.7528			
T = 303.15 K											
0.9008	0.769 09	0.3790	0.4810	0.776 92	0.7400	0.7004	0.771 90	0.7088	0.2488	0.793 63	0.5010
0.8329	0.769 81	0.5277	0.4038	0.778 97	0.6944	0.6285	0.773 26	0.7663	0.1668	0.786 33	0.3481
0.7698	0.770 64	0.6397	0.3273	0.781 24	0.6073	0.5546	0.774 99	0.7717			
Cyclohexane (1) + 1-Propanol (2)											
T = 298.15 K											
0.1548	0.792 30	0.1992	0.5176	0.780 50	0.4103	0.2794	0.787 58	0.3016	0.7887	0.775 18	0.3539
0.2073	0.790 22	0.2453	0.6033	0.778 50	0.4190	0.3101	0.786 46	0.3297	0.8388	0.774 53	0.3127
0.2408	0.788 88	0.2811	0.7404	0.775 90	0.3853	0.4866	0.781 25	0.4082	0.9018	0.773 89	0.2413
T = 303.15 K											
0.1548	0.788 06	0.2095	0.5176	0.775 98	0.4252	0.2794	0.793 21	0.3168	0.7887	0.770 51	0.3677
0.2073	0.785 91	0.2594	0.6033	0.773 97	0.4283	0.3101	0.782 10	0.3421	0.8388	0.769 79	0.3314
0.2408	0.784 57	0.2931	0.7404	0.771 25	0.3998	0.4866	0.776 80	0.4169	0.9018	0.769 18	0.2509
Cyclohexane(1) + 2-Propanol (2)											
T = 298.15 K											
0.1755	0.776 36	0.3061	0.5773	0.771 33	0.6073	0.4129	0.772 69	0.5452	0.7451	0.771 10	0.5373
0.2727	0.774 54	0.4303	0.6422	0.771 09	0.5989	0.4388	0.772 35	0.5686	0.8410	0.771 55	0.4203
0.3397	0.773 53	0.4968	0.7027	0.770 99	0.5764	0.4943	0.771 83	0.5960	0.8945	0.771 91	0.3386
0.5193	0.771 65	0.6026									
T = 303.15 K											
0.1755	0.771 85	0.3260	0.5773	0.766 48	0.6513	0.4129	0.767 94	0.5835	0.7451	0.766 24	0.5755
0.2727	0.769 88	0.4633	0.6422	0.766 26	0.6381	0.4388	0.767 58	0.6085	0.8410	0.766 68	0.4546
0.3397	0.768 84	0.5309	0.7027	0.766 11	0.6194	0.4943	0.767 00	0.6412	0.8945	0.767 08	0.3643
0.5193	0.766 82	0.6473									
Ethanoic Acid (1) + 1-Propanol (2)											
T = 298.15 K											
0.1021	0.819 91	−0.0571	0.5829	0.929 38	−0.2197	0.3558	0.874 80	−0.1872	0.7871	0.983 31	−0.1668
0.1894	0.838 14	−0.1137	0.6540	0.947 68	−0.2153	0.4330	0.892 77	−0.2097	0.8517	1.001 34	−0.1284
0.2707	0.855 66	−0.1498	0.7233	0.965 93	−0.1918	0.5097	0.911 16	−0.2168	0.9108	1.018 32	−0.0871
T = 303.15 K											
0.1021	0.815 71	−0.0510	0.5829	0.924 47	−0.2169	0.3558	0.870 20	−0.1791	0.7871	0.978 01	−0.1632
0.1894	0.833 74	−0.1011	0.6540	0.942 61	−0.2102	0.4330	0.888 04	−0.2013	0.8517	0.995 91	−0.1246
0.2707	0.851 17	−0.1398	0.7233	0.960 76	−0.1890	0.5097	0.906 31	−0.2091	0.9108	1.012 81	−0.0857

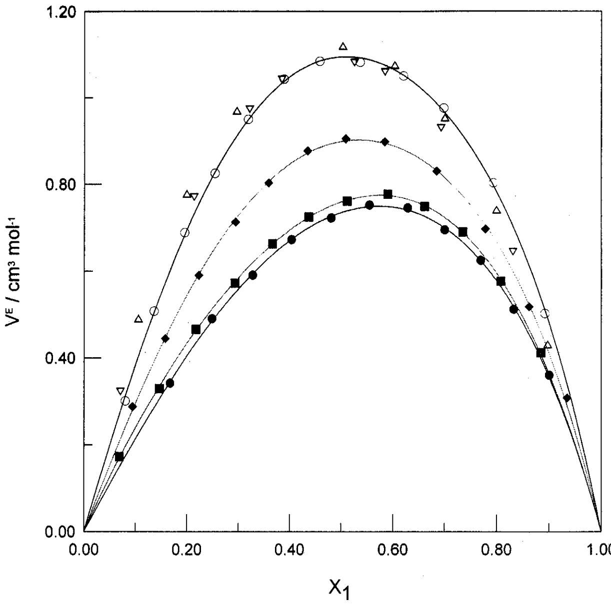

Figure 1. Excess volumes of binary systems at 298.15 K: cyclohexane (1) + 2-propanone (2): ▽, Puri et al. (1974); △, Radojkovic et al. (1977); ○, this work; ◆, cyclohexane (1) + 2-butanol (2); ■, cyclohexane (1) + 3-pentanone (2); ●, cyclohexane (1) + 4-methyl-2-pentanone (2); —, correlated.

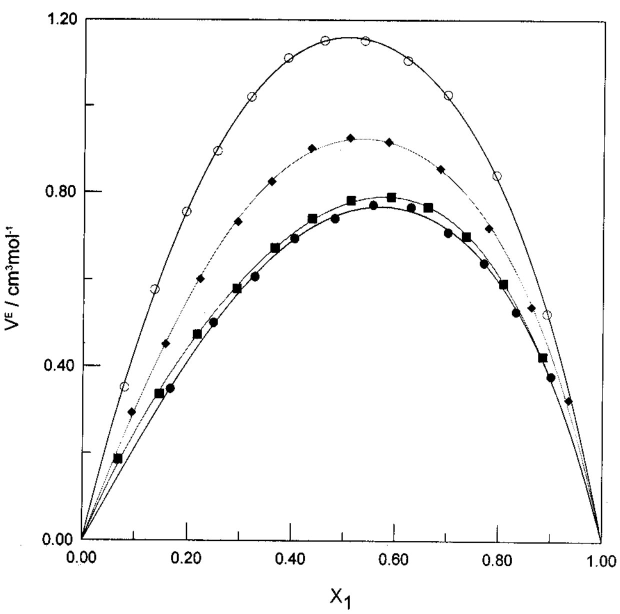

Figure 2. Excess volumes of binary systems at 303.15 K: ○, cyclohexane (1) + 2-propanone (2); ◆, cyclohexane (1) + 2-butanone (2); ■, cyclohexane (1) + 3-pentanone (2); ●, cyclohexane (1) + 4-methyl-2-pentanone (2); —, correlated.

The experimental excess molar volumes of all seven mixtures at 298.15 K and 303.15 K are listed in Table 2. The excess molar volume was calculated by the following equation

$$V^{\mathrm{E}} = \frac{(x_1M_1 + x_2M_2)}{\rho_{\mathrm{m}}} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \quad (1)$$

where x_i, M_i, and $\rho_i = 1, 2$, are the mole fractions, molar masses, and densities of the constituent components, respectively, and ρ_m is the density of the mixture.

The experimental excess molar volumes were correlated by Redlich−Kister equation

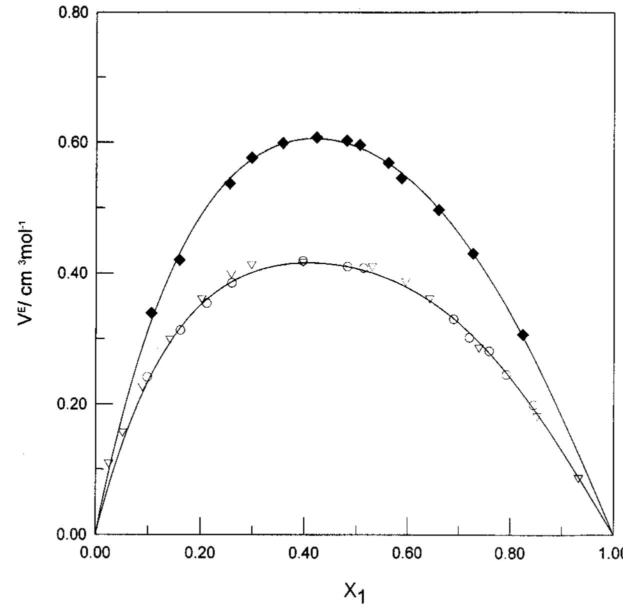

Figure 3. Excess volumes of binary systems at 298.15 K: cyclohexane (1) + 1-propanol (2): ○, this work; ▽, Janssens and Ruel (1972); ◆, cyclohexane (1) + 2-propanol (2); —, correlated.

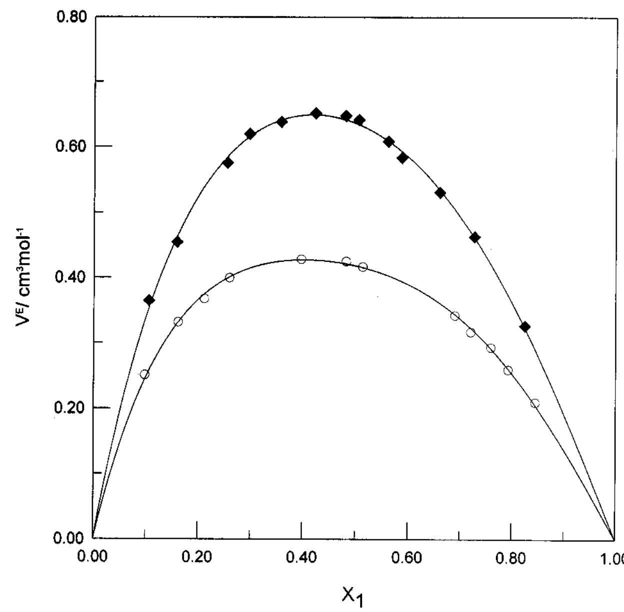

Figure 4. Excess volumes of binary systems at 303.15 K: ○, cyclohexane (1) + 1-propanol (2); ◆, cyclohexane (1) + 2-propanol (2); —, correlated.

$$V^{\mathrm{E}}/(x_1x_2) = A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 + A_3(x_1 - x_2)^3 \quad (2)$$

where the parameters given in Table 3 were determined by nonweighed least-squares fit.

The figures showing the experimental data and the correlated values are given in Figures 1−5. Figure 1 shows the excess volumes of mixtures of cyclohexane with 2-propanone, 2-butanone, 3-pentanone, and 4-methyl-2-pentanone at 298.15 K. In this figure, the literature values of the cyclohexane + 2-propanone mixture of Puri et al. (1974) and of Radojkovic et al. (1977) are also shown. This figure shows the positive excess volumes of mixtures of this group and the good agreement of experimental and correlated values. The excess volumes of the same mixtures of the temperature of 303.15 K were given in Figure 2. Similar to Figure 1, this same group of mixtures also exhibit

Table 3. Parameters A_k of Equation 2 for Excess Molar Volume

mixture	T/K	A_0	A_1	A_2	A_3	$\sigma(V^E)$/cm^3·mol^{-1}
cyclohexane (1)	298.15	4.381 91	−0.152 56	0.671 51	−0.835 17	0.0076
+ 2-propanone (2)	303.15	4.637 81	−0.900 50	0.892 07	−0.517 41	0.0067
cyclohexane (1)	298.15	3.595 98	−0.413 36	0.528 45	−0.614 34	0.0090
+ 2-butanone (2)	303.15	3.683 71	−0.403 72	0.583 87	−0.815 67	0.0099
cyclohexane (1)	298.15	3.038 07	−0.809 31	0.503 03	−0.095 41	0.0038
+ 3-pentanone (2)	303.15	3.092 96	−0.863 96	0.551 26	−0.015 81	0.0064
cyclohexane (1)	298.15	2.945 07	−0.786 09	0.365 82	−0.327 83	0.0053
+ 4-methyl-2-pentanone (2)	303.15	3.016 52	−0.749 80	0.359 92	−0.567 35	0.0072
cyclohexane (1)	298.15	1.628 63	−0.376 44	0.616 06	−0.552 35	0.0058
+ 1-propanol (2)	303.15	1.673 29	0.365 85	0.731 34	0.615 06	0.0046
cyclohexane (1)	298.15	2.372 43	0.607 30	0.588 62	0.477 49	0.0069
+ 2-propanol (2)	303.15	2.542 76	−0.639 32	0.634 00	−0.583 43	0.0078
ethanoic acid (1)	298.15	−0.875 57	0.195 24	0.036 69	0.094 51	0.0026
+ 1-propanol (2)	303.15	−0.850 00	0.236 95	0.084 13	0.083 40	0.0024

[a] $\sigma(V^E)$: standard deviation.

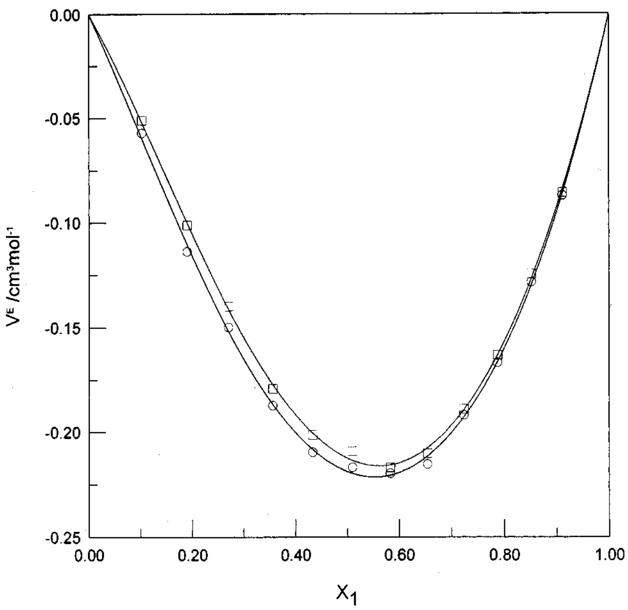

Figure 5. Excess volumes of ethanoic acid (1) + 1-propanol (2): ○, at 298.15 K; □ at 303.15 K; —, correlated.

positive excess volumes. Figure 3 shows the excess volumes of cyclohexane + 1-propanol and cyclohexane + 2-propanol mixtures at the temperature of 298.15 K. The literature values of Janssens and Ruel (1972) are also included in this figure. This figure shows the positive excess volume of these two mixtures. The same mixtures at temperature of 303.15 K are given in Figure 4. We can also observe that the excess volumes are larger at the higher temperature for the mixtures shown in these figures. The excess volumes of the last mixture, consisting of an associating component and a polar component, ethanoic acid + 1-propanol at 298.15 K and 303.15 K, are given in Figure 5. This mixture exhibits negative excess molar volume, which is the opposite behavior compared with that shown for the previous mixtures.

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