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Excess Molar Volume and Apparent Molar Volume of Binary Mixtures of 2-Methyl-3-buten-2-ol with 1-Alcohol at 298.15 K*

LIU Dixia(刘迪霞), LI Haoran(李浩然), DENG Dongshun(邓东顺) and HAN Shijun(韩世钧)**
Department of Chemistry, Zhejiang University, Hangzhou 310027, China

Abstract Excess molar volumes (V_m^E) of binary mixtures of 2-methyl-3-buten-2-ol [$CH_3C(OH)(CH_3)CHCH_2$] with four 1-alcohols: methanol, ethanol, 1-propanol and 1-butanol at 298.15 K and atmospheric pressure are derived from density measurements with a vibrating-tube densimeter. All the excess volumes are negative in the systems over the entire composition range. The results are correlated with the Redlich-Kister equation. The effects of chain length of 1-alcohols on V_m^E are discussed. The apparent molar volumes of 2-methyl-3-buten-2-ol and 1-alcohols are calculated respectively.

Keywords excess molar volume, binary mixture, 2-methyl-3-buten-2-ol, 1-alcohol, apparent molar volume

1 INTRODUCTION

The development of synthetic vitamin production involves some new substances. Unfortunately, the data on the properties of these substances are often incomplete or even unavailable[1].

In this paper, the excess molar volumes V_m^E of 2-methyl-3-buten-2-ol [$CH_3C(OH)(CH_3)CHCH_2$], an important intermediate for the syntheses of vitamins, with four 1-alcohols: methanol, ethanol, propanol and butanol are measured at 298.15 K and atmospheric pressure from density measurements with a vibrating densimeter. The V_m^E values are correlated with the Redlich-Kister equation[2]. Both the apparent molar volumes of 2-methyl-3-buten-2-ol and 1-alcohols are calculated.

2 EXPERIMENTAL

2.1 Materials

2-Methyl-3-buten-2-ol (97.5%, industrial grade) was distilled by using a 150 cm-length column under the atmospheric pressure. The stable boiling fraction of the distillate was collected in a yellow bottle. 1-Alcohols (analytical reagent grade, Shanghai Chemical Co.) were purified by the methods described by Rao and Naidu[3]. Pure materials were carefully dried with molecular sieves (0.3 nm, from Shanghai Chemical Co.). The purities of the materials were determined by gas chromatography: 2-methyl-3-buten-2-ol, 99.60%(by mass), methanol, 99.99%(by mass), ethanol, 99.98%(by mass), propanol, 99.97%(by mass) and butanol, 99.98%(by mass). Refractive indices were measured with an Abbe type refractometer (WZS-I model, made in Shanghai) with a precision of ±0.0001. The measured physical properties of the pure materials are included in Table 1. They are in good agreement with the literature values (Table 1).

Table 1 Physical properties of the materials at 298.15 K

Material	Density, g·cm^{-3}		Refractive index	
	exp.	lit.	exp.	lit.
2-methyl-3-buten-2-ol	0.82338	0.8234[1] (293.15 K)	1.4152	1.4170[1] (293.15 K)
methanol	0.78667	0.78664[4]	1.3272	1.32652[4]
ethanol	0.78496	0.78509[4]	1.3592	1.35941[4]
1-propanol	0.79965	0.79976[5]	1.3830	1.38324[6]
1-butanol	0.80590	0.8058[4]	1.3968	1.39741[4]

2.2 Density measurements

Densities of the pure materials and mixtures were measured with an Anton Paar DMA 602 densimeter with an accuracy of ±0.00002 g·cm^{-3}. Ethanol was used for rinsing the cell tube between measurements. Before each series of measurements the instrument was calibrated with doubly distilled and degassed water and "vacuum". In the measurements all the liquids were partially degassed. The densimeter and refractometer were thermostated to temperatures with a precision of ±0.01 K by a circulating-water bath. All mixtures were prepared by directly weighing the constituent components in small oninostyle vessels in order to prevent evaporation. The error in the final mole fraction is estimated to be less than ±0.0001 from the measured apparent masses of the components. For more details see references[7–9].

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** To whom correspondence should be addressed. E-mail: lihr@zju.edu.cn

3 RESULTS AND DISCUSSION

3.1 Excess molar volume

The density ρ and excess molar volumes V_m^E for four binary systems containing 2-methyl-3-buten-2-ol with methanol, ethanol, propanol and butanol for a number of mole fractions at 298.15 K and atmospheric pressure are listed in Table 2. The values of V_m^E were calculated according to the fundamental equation

$$V_m^E = M_1 x_1 (1/\rho_{mix} - 1/\rho_1) + M_2 x_2 (1/\rho_{mix} - 1/\rho_2) \quad (1)$$

The results of V_m^E for each mixture are fitted to the Redlich-Kister polynomial equation

$$V_m^E = x_1 x_2 \sum_{i=1}^{m} K_i (x_1 - x_2)^{i-1} \quad (2)$$

The coefficients of Eq. (2) were obtained by a modified Powell optimization method[10] by examining the standard deviation

$$\sigma = \left[\sum_{i=1}^{n} (V_{exp}^E - V_{cal}^E)_i^2 / (n - m) \right]^{1/2} \quad (3)$$

The coefficients K_i in Eq. (2) and corresponding standard deviations σ are given in Table 3.

Figure 1 shows the values of V_m^E for four binary systems at 298.15 K as a function of the mole fraction x_1 of 2-methyl-3-buten-2-ol. For all the systems investigated, the values of V_m^E are negative over the whole mole fraction range. Fig. 1 also shows that the values of $|V_m^E|$ decrease in the order of increasing size of the alcohol molecule.

We note that V_m^E containing 1-alcohols is the result of several opposing effects: decreasing in self-association and physical interactions(dipole-dipole) between alcohol multimers and monomers leads to an increase of volume; the decrease of volume is obtained by changes of free volume and interstitial accomodation[11]. It is more important in mixtures containing short alcohol molecules. In addition, the new hydrogen bonds created contribute negatively to V_m^E. For the mixtures under study, the contribution from the interstitial accomodation and new hydrogen bonds might be negative enough so that $V_m^E < 0$.

Table 2 Excess molar volumes V_m^E for 2-methyl-3-buten-2-ol (x_1) + 1-alcohol (x_2) at 298.15 K and atmospheric pressure

Methanol (x_2)			Ethanol (x_2)			1-Propanol (x_2)			1-Butanol (x_2)		
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}
0.0263	0.78943	−0.0323	0.0459	0.79019	−0.0566	0.0461	0.80180	−0.0547	0.0673	0.80767	−0.0588
0.0895	0.79510	−0.1078	0.0958	0.79360	−0.1236	0.0951	0.80365	−0.1152	0.1086	0.80866	−0.1049
0.1526	0.79996	−0.1891	0.1475	0.79683	−0.1889	0.1600	0.80604	−0.2001	0.1524	0.80970	−0.1547
0.2042	0.80354	−0.2651	0.1885	0.79925	−0.2427	0.2025	0.80745	−0.2459	0.2021	0.81079	−0.2021
0.2511	0.80632	−0.3257	0.2920	0.80469	−0.3676	0.2522	0.80903	−0.2985	0.2521	0.81191	−0.2527
0.3058	0.80914	−0.3910	0.3676	0.80812	−0.4479	0.2968	0.81034	−0.3381	0.2929	0.81277	−0.2904
0.3469	0.81094	−0.4309	0.4184	0.81009	−0.4864	0.3395	0.81157	−0.3785	0.3619	0.81407	−0.3379
0.4022	0.81323	−0.4927	0.4422	0.81091	−0.4978	0.3956	0.81302	−0.4187	0.4493	0.81559	−0.3858
0.4528	0.81501	−0.5394	0.4986	0.81265	−0.5200	0.4444	0.81421	−0.4519	0.4998	0.81633	−0.3992
0.5041	0.81651	−0.5740	0.5551	0.81432	−0.5357	0.4973	0.81531	−0.4703	0.5573	0.81713	−0.4101
0.5438	0.81751	−0.5948	0.5957	0.81527	−0.5310	0.5411	0.81615	−0.4811	0.5957	0.81760	−0.4111
0.6187	0.81905	−0.6157	0.6551	0.81654	−0.5187	0.6046	0.81719	−0.4825	0.6560	0.81817	−0.3920
0.6503	0.81951	−0.6109	0.6914	0.81718	−0.4999	0.6410	0.81768	−0.4721	0.7151	0.81864	−0.3647
0.7085	0.82014	−0.5864	0.7495	0.81803	−0.4560	0.6869	0.81821	−0.4514	0.7402	0.81880	−0.3481
0.7851	0.82052	−0.5114	0.7818	0.81827	−0.4082	0.7305	0.81861	−0.4215	0.8127	0.81910	−0.2808
0.8474	0.82043	−0.4091	0.8220	0.81862	−0.3548	0.7815	0.81889	−0.3660	0.8252	0.81916	−0.2696
0.8911	0.82021	−0.3181	0.8930	0.81901	−0.2375	0.8642	0.81914	−0.2518	0.9120	0.81923	−0.1537
0.9343	0.81979	−0.2010				0.8934	0.81917	−0.2043	0.9325	0.81913	−0.1118

Table 3 Coefficients K_i and standard deviations (σ) of Eq. (2) for the binary systems of 2-methyl-3-buten-2-ol + 1-alcohol at 298.15 K and atmospheric pressure

2-Methyl-3-buten-2-ol +	K_0	K_1	K_2	K_3	K_4	σ, cm^3·mol^{-1}
methanol	−2.28446	−1.26817	−0.27396	0.12674	0.38334	0.00262
ethanol	−2.09656	−0.67701	0.14210	0.01202	0.16672	0.00358
1-propanol	−1.88835	−0.6246	0.04337	0.23500	0.26507	0.00197
1-butanol	−1.60632	−0.46651	0.02177	−0.05675	0.31126	0.00255

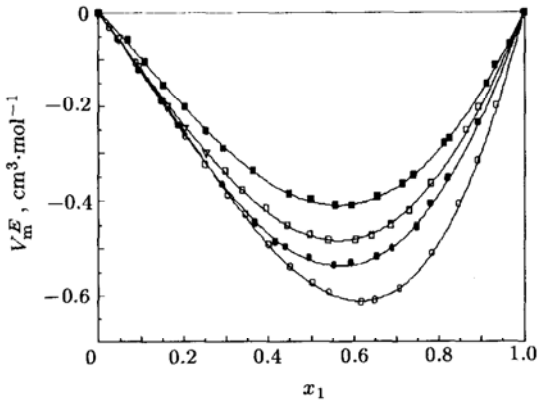


Figure 1 Excess molar volumes for 2-methyl-3-buten-2-ol (x_1) + 1-alcohol (x_1) at 298.15 K and atmospheric pressure
○ methanol; ● ethanol; □ 1-propanol; ◆ 1-butanol

For the systems in our study, with the length of 1-alcohol increasing, the molar fraction of —OH group in alcohol molecular surface area decreases obviously. It leads to the retract of volume resulted from the decrease of the hydrogen-bond between 1-alcohol and 2-methyl-3-buten-2-ol , so the values of $|V_m^E|$ decrease with the size of the alcohol molecule. This also results in the V_m^E curves shifting to the region rich in 2-methyl-3-buten-2-ol and increasing symmetry with the size of 1-alcohol molecule.

3.2 Apparent molar volume

The apparent molar volumes V_1^ϕ of 2-methyl-3-buten-2-ol and V_2^ϕ of 1-alcohols can be calculated by the following equations

$$V_1^\phi = M_1/\rho_{mix} + M_2(1/\rho_{mix} - 1/\rho_2)x_2/x_1 \quad (4)$$

$$V_2^\phi = M_2/\rho_{mix} + M_1(1/\rho_{mix} - 1/\rho_1)x_1/x_2 \quad (5)$$

The apparent molar volumes V_1^ϕ of 2-methyl-3-buten-2-ol and V_2^ϕ of 1-alcohols for the four binary mixtures at 298.15 K are listed in Tables 4 and 5.

Figure 2 presents V_1^ϕ and V_2^ϕ as a function of the mole fraction x_1 and x_2 for the four binary mixtures respectively. It can be seen that the main difference between V_1^ϕ and V_2^ϕ is the change in curvature. The curves of V_2^ϕ are nearly horizontal lines. The reason may be that the changes of associations (including self-association and hetero-association) are insignificant for the 1-alcohols, the number of hydrogen bonds can be exactly compensated by the new hydrogen bonds formed after mixed.

As to 2-methyl-3-buten-2-ol in four binary systems, the relationship between V_1^ϕ and x_1 can be expressed with Eq. (6)[12,13]

$$V_1^\phi = \Phi_1^0 + B_1x_1 + B_2x_1^2 + \cdots \quad (6)$$

The coefficients B_1, B_2 and standard deviations σ' of second-order correlation are listed in Table 6.

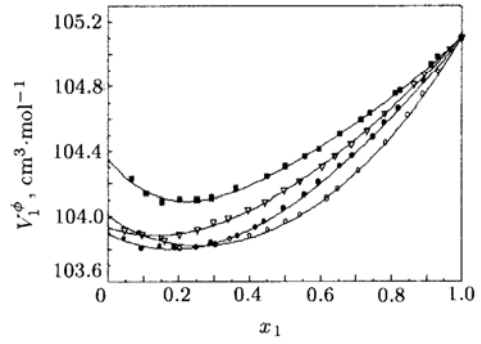
Comparing to 1-alcohols, the changes of associations in 2-methyl-3-buten-2-ol is larger, probably becauses of its charge interaction between hydroxy group and double bond, the number of hydrogen bonds created after mixed is larger than the broken ones. Therefore, the values of V_1^ϕ first decrease to a

Table 4 Apparent molar volumes V_1^ϕ of 2-methyl-3-buten-2-ol for the binary mixtures of 2-methyl-3-buten-2-ol(x_1) + 1-alcohol(x_2) at 298.15 K and atmospheric pressure

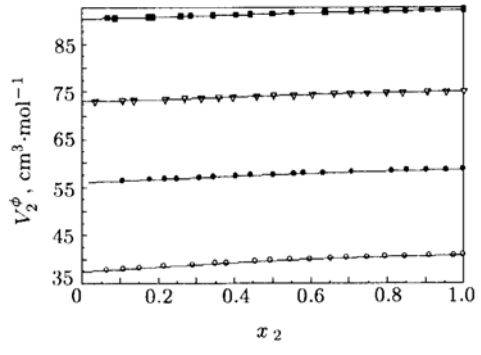
Methanol (x_2)		Ethanol (x_2)		1-Propanol (x_2)		1-Butanol (x_2)	
x_1	V_1^ϕ cm^3·mol^{-1}	x_1	V_1^ϕ cm^3·mol^{-1}	x_1	V_1^ϕ cm^3·mol^{-1}	x_1	V_1^ϕ cm^3·mol^{-1}
0.0895	103.8975	0.0459	103.8584	0.0461	103.9162	0.0673	104.2289
0.1526	103.8630	0.0958	103.8024	0.0951	103.8900	0.1086	104.1354
0.2042	103.8036	0.1475	103.8122	0.1600	103.8516	0.1524	104.0870
0.2511	103.8049	0.1885	103.8052	0.2025	103.8879	0.2021	104.1023
0.3058	103.8231	0.2920	103.8342	0.2522	103.9183	0.2521	104.0997
0.3469	103.8600	0.3676	103.8744	0.2968	103.9627	0.2929	104.1106
0.4022	103.8769	0.4184	103.9304	0.3395	103.9870	0.3619	104.1683
0.4528	103.9109	0.4422	103.9672	0.3956	104.0435	0.4493	104.2433
0.5041	103.9635	0.4968	104.0461	0.4444	104.0853	0.4998	104.3033
0.5438	104.0081	0.5551	104.1278	0.4973	104.1563	0.5573	104.3662
0.6187	104.1068	0.5957	104.2014	0.5411	104.2128	0.5957	104.4120
0.6503	104.1627	0.6551	104.3012	0.6046	104.3038	0.6560	104.5045
0.7085	104.2743	0.6914	104.3698	0.6410	104.3655	0.7151	104.5919
0.7851	104.4506	0.7495	104.4845	0.6869	104.4448	0.7402	104.6317
0.8474	104.6192	0.7818	104.5708	0.7305	104.5249	0.8127	104.7565
0.8911	104.7450	0.8220	104.6613	0.7815	104.6337	0.8252	104.7753
0.9343	104.8869	0.8930	104.8269	0.8642	104.8106	0.9120	104.9335
				0.8934	104.8733	0.9325	104.9821
				0.9658	105.0308		

Table 5 Apparent molar volumes V_2^{ϕ} of 1-alcohols for binary mixtures of 2-methyl-3-buten-2-ol(x_1) +1-alcohol(x_2) at 298.15 K and atmospheric pressure

Methanol (x_2)		Ethanol (x_2)		1-Propanol (x_2)		1-Butanol (x_2)	
x_1	V_2^{ϕ} cm^3·mol^{-1}	x_1	V_2^{ϕ} cm^3·mol^{-1}	x_1	V_2^{ϕ} cm^3·mol^{-1}	x_1	V_2^{ϕ} cm^3·mol^{-1}
0.0657	37.6663	0.1070	56.2516	0.0342	73.0974	0.0675	90.2845
0.1089	37.8033	0.1780	56.5118	0.1066	73.1928	0.0880	90.1939
0.1526	38.0456	0.2182	56.6433	0.1358	73.2554	0.1748	90.3978
0.2149	38.3462	0.2505	56.6990	0.2185	73.4351	0.1873	90.4401
0.2915	38.7143	0.3086	56.9062	0.2695	73.5463	0.2598	90.5999
0.3497	38.9786	0.3449	57.0252	0.3131	73.6685	0.2849	90.6595
0.3813	39.1111	0.4043	57.2195	0.3590	73.7952	0.3440	90.8003
0.4562	39.4219	0.4449	57.3308	0.3954	73.8900	0.4043	90.9228
0.4959	39.5683	0.5032	57.5040	0.4589	74.0617	0.4427	91.0133
0.5472	39.7400	0.5578	57.6465	0.5027	74.1747	0.5002	91.1416
0.5978	39.9017	0.5816	57.7033	0.5556	74.2968	0.5507	91.2390
0.6531	40.0660	0.6324	57.8328	0.6044	74.4175	0.6381	91.4101
0.6942	40.1626	0.7080	58.0233	0.6605	74.5371	0.7071	91.5290
0.7489	40.2908	0.8115	58.2450	0.7032	74.6293	0.7479	91.6017
0.7958	40.3927	0.8525	58.3231	0.7478	74.7110	0.7979	91.6864
0.8474	40.5026	0.9042	58.4086	0.7975	74.8019	0.8476	91.7571
0.9105	40.6074	0.9541	58.4864	0.8400	74.8719	0.8914	91.8219
0.9737	40.6927			0.9049	74.9828	0.9327	91.8766
				0.9539	75.0529		



(a)



(b)

Figure 2 Apparent molar volumes V_1^{ϕ} of 2-methyl-3-buten-2-ol (a) and V_2^{ϕ} of 1-alcohols (b) for 2-methyl-3-buten-2-ol(x_1) + 1-alcohol (x_2) at 298.15 K and atmospheric pressure

○ methanol; ● ethanol; ▽ 1-propanol; ◆ 1-butanol

minimum as x_1 increases [Fig. 2(a)], then increase to the molar volume value of pure 2-methyl-3-buten-2-ol. The reason might be that the effect of high-rank concentration terms in Eq. (6) is predominent and the effect of hydrogen bonds decreases after that minimum.

Table 6 Coefficients B_1, B_2, and standard deviations σ' of second-order correlation of Eq. (6) for the binary systems of 2-methyl-3-buten-2-ol + 1-alcohol at 298.15 K and atmospheric pressure

2-methyl-3-buten-2-ol +	B_1	B_2	σ' cm^3·mol^{-1}
methanol	−1.26081	2.36920	0.01258
ethanol	−0.46301	1.75471	0.02049
1-propanol	−0.13590	1.38561	0.01811
1-butanol	−0.45165	1.43162	0.03347

As mentioned above, we know that for each of the four binary systems, the number of hydrogen bonds increases after mixed, which contributes negatively to V_m^E. This is consistent with the fact of $V_m^E < 0$ (Section 3.1).

4 CONCLUSIONS

Excess molar volumes (V_m^E) of binary mixtures of 2-methyl-3-buten-2-ol with four 1-alcohols: methanol, ethanol, 1-propanol and 1-butanol were determined. The results were correlated with the Redlich-Kister equation. Because of the effect of hydrogen bonds and free volume, all the excess volumes are negative in the systems over the entire composition range and change regularly with the length of 1-alcohols. The apparent molar volumes of 2-methyl-3-buten-2-ol and 1-alcohols were calculated respectively. The reasons of the difference between V_1^{ϕ} and V_2^{ϕ} curves were discussed.

NOMENCLATURE

B_1, B_2	the second and third Virial coefficients
K_0—K_4	polynomial coefficients in Eq. (2)
M_1, M_2	molar weight of 2-methyl-3-buten-2-ol and 1-alcohols
m	polynomial degree in Eq. (2)
n	number of experimental data
V_m^E	excess molar volume, $cm^3 \cdot mol^{-1}$
$\|V_m^E\|$	absolute value of the excess molar volume, $cm^3 \cdot mol^{-1}$
V_1^ϕ, V_2^ϕ	apparent molar volume of 2-methyl-3-buten-2-ol and 1-alcohols, $cm^3 \cdot mol^{-1}$
x_1, x_2	mole fraction of 2-methyl-3-buten-2-ol and 1-alcohols
ρ_{mix}	density of the mixture, $g \cdot cm^{-3}$
ρ_1, ρ_2	density of 2-methyl-3-buten-2-ol and 1-alcohols, $g \cdot cm^{-3}$
σ	standard deviation of Eq. (2)
σ'	standard deviation of the second-order correlation in Eq. (6)
Φ_1^0	apparent molar volume of 2-methyl-3-buten-2-ol in infinite dilution, $cm^3 \cdot mol^{-1}$

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