Short Articles

Densities and Viscosities of Binary Liquid Mixtures of 2-Butanone with Branched Alcohols at (293.15 to 313.15) K

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Densities and viscosities of the binary mixtures of 2-butanone with 2-propanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-butanol were measured over the entire mole fractions at (293.15, 298.15, 303.15, 308.15, and 313.15) K. Using the experimental values of densities, excess molar volumes V^E were calculated. The results were discussed in terms of molecular interactions.

Introduction

Physicochemical properties such as densities and viscosities of pure liquids and of their binary liquid mixtures over the whole composition range measured at several temperatures are useful for a full understanding of their thermodynamic and transport properties as well as practical chemical engineering purposes. On the other hand, excess thermodynamic function and deviation of the nonthermodynamic function of binary liquid mixtures are of fundamental use for understanding the types of interactions between the components of the mixture.[1−3]

2-Butanone is an interesting solvent widely employed in scientific studies and industrial applications, especially for the solvating properties associated with its own character as an aprotic and protophilic medium,[4] a high dipole moment (μ_1 = 2.75 D), and relatively low static dielectric constant (ε = 18.51) at 20 °C.

Alcohols are versatile solvents used in the separation of saturated and unsaturated hydrocarbons and in pharmaceutical synthesis and serve as solvents for many polymers. Alcohols are polar and self-associated through hydrogen bonding in the state.[5] In this study, we have reported the densities and viscosities of 2-butanone with branched alcohols as 2-propanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-butanol at various temperatures T = (293.15, 298.15, 303.15, 308.15, and 313.15) K over the entire composition range.

Experimental Section

Materials. 2-Butanone (SD fine AR, ≥ 98 %) was doubly distilled over anhydrous potassium carbonate/sodium carbonate to eliminate traces of acids and to further reduce the water content, and the four branched alcohols were purified by the standard methods.[6,7] All the liquids were filtered and distilled at atmospheric pressure. The middle fraction collected of all the liquids was stored over 4 Å type molecular sieves. The triple distilled liquids invariably were used. All the chemicals were degassed before use. The purity of purified chemicals was checked by comparing the measured densities and viscosities with those reported in the literature.[7,8] The measured values are included in Table 1 along with the literature values. The experimental and literature values show good agreement.

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Table 1. Comparison of Experimental and Literature Values of Density ρ and Viscosity η for Pure Components at T = (293.15 to 313.15) K[a]

		ρ/g·cm^{-3}		η/mPa·s	
liquid	T/K	exptl	lit.[6]	exptl	lit.[6]
2-butanone	293.15	0.80492	0.8049	0.3956	0.399
	298.15	0.79970	0.7997	0.2828	0.378
	303.15	0.79481	0.7946	0.2666	0.366
	308.15	0.78978	-	0.2601	-
	313.15	0.78432	-	0.2545	-
2-propanol	293.15	0.78545	0.78545	2.2256	-
	298.15	0.78126	0.78126	1.9102	2.0436
	303.15	0.77797	-	1.7370	1.767
	308.15	0.77259	-	1.5242	-
	313.15	0.76832	-	1.3472	-
2-methyl-1-propanol	293.15	0.80168	0.8016	4.0366	-
	298.15	0.79780	0.7978	3.3297	3.3330
	308.15	0.79416	-	2.8752	-
	308.15	0.79006	-	2.4207	-
	313.15	0.78670	-	1.9666	-
2-butanol	293.15	0.80648	0.80652	3.6316	3.632
	298.15	0.80235	0.80241	2.9975	2.998
	308.15	0.79896	-	2.4978	2.498
	308.15	0.79418	-	2.0542	-
	313.15	0.79007	-	1.7989	-
2-methyl-2-butanol	293.15	0.80961	0.8096	5.1080	-
	298.15	0.80501	0.8050	4.4740	3.548
	303.15	0.80041	-	3.9086	-
	308.15	0.79581	-	3.3871	-
	313.15	0.79121	-	2.9086	-

[a] Ref 6. Riddick and Bunger (1986).

Measurements. The binary liquid mixtures were prepared by mixing known masses of pure liquids in airtight-stoppered bottles to minimize the evaporation losses. All measurements of mass were performed on a Mettler one-pan balance (E-METTLER, ZURICH), which allows reading the fifth decimal digit, with a precision of ± 0.05 mg. The uncertainty in the mole fractions of the mixtures was estimated to be ± $5 \cdot 10^{-5}$.

Densities of pure components and their mixtures were measured using the single arm capillary pycnometer having a bulb volume of approximately 5 cm^3 and a capillary bore with an internal diameter of 0.75 mm. The uncertainty in the density measurements was found to be ± $5 \cdot 10^{-5}$ g·cm^{-3}.

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Table 2. Densities ρ for 2-Butanone (1) + 2-Propanol (2) from T = (293.15 to 313.15) K

	ρ/g·cm^{-3}				
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
0.0000	0.78545	0.78126	0.77797	0.77259	0.76832
0.0562	0.78640	0.78234	0.77890	0.77352	0.76921
0.1136	0.78747	0.78331	0.77985	0.77458	0.77017
0.1724	0.78854	0.78436	0.78081	0.77558	0.77113
0.2326	0.78967	0.78546	0.78182	0.77664	0.77212
0.2941	0.79083	0.78659	0.78285	0.77770	0.77313
0.3571	0.79205	0.78774	0.78391	0.77880	0.77416
0.4217	0.79329	0.78895	0.78501	0.77992	0.77521
0.4878	0.79460	0.79018	0.78614	0.78107	0.77627
0.5555	0.79596	0.79144	0.78729	0.78224	0.77737
0.6250	0.79735	0.79274	0.78849	0.78344	0.77848
0.6962	0.79879	0.794.08	0.78970	0.78466	0.77961
0.7692	0.80026	0.79545	0.79095	0.78591	0.78076
0.8442	0.80760	0.79686	0.79221	0.78718	0.78193
0.9211	0.80330	0.79830	0.79351	0.78848	0.78312
1.0000	0.80492	0.79970	0.79481	0.78978	0.78432

Table 3. Densities ρ for 2-Butanone (1) + 2-Methyl-1-propanol (2) from T = (293.15 to 313.15) K

	ρ/g·cm^{-3}				
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
0.0000	0.80168	0.79780	0.79416	0.79006	0.78670
0.0684	0.80190	0.79793	0.79421	0.79004	0.78654
0.1365	0.80211	0.79806	0.79425	0.79003	0.78639
0.2044	0.80232	0.79818	0.79429	0.79000	0.78622
0.2721	0.80252	0.79829	0.79432	0.78998	0.78606
0.3395	0.80272	0.79841	0.79436	0.78995	0.78589
0.4066	0.80292	0.79852	0.79439	0.78992	0.78573
0.4735	0.80313	0.79863	0.79442	0.78989	0.78556
0.5402	0.80333	0.79875	0.79446	0.78987	0.78540
0.6066	0.80354	0.79887	0.79449	0.78985	0.78523
0.6727	0.80375	0.79899	0.79453	0.78983	0.78508
0.7387	0.80397	0.79912	0.79458	0.78982	0.78492
0.8044	0.80420	0.79925	0.79463	0.78981	0.78477
0.8698	0.80443	0.79940	0.79468	0.78980	0.78462
0.9350	0.80467	0.79954	0.79474	0.78979	0.78447
1.0000	0.80492	0.79970	0.79481	0.78978	0.78432

Viscosity measurements were performed by using Schott Gerate (AVS 350) viscosity measuring equipment with a series of Ubbelhode viscometers. The experimental uncertainty of the viscosity measurements at each temperature and solution was ± 0.002 mPa·s. For all the measurements, temperature was controlled by circulating the water through an ultra thermostat JULABO F-25 (made in Germany) which has an accuracy ± 0.02 °C.

Results

Tables 2 to 9 list the densities ρ, and viscosities η, of the binary mixtures of 2- butanone + 2-propanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-butanol.

Excess molar volumes, V^E, were calculated[8,9] from the measured densities, ρ, by using the equation

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

where ρ is the density of the mixture and M_1, x_1, ρ_1 and M_2, x_2, ρ_2 are the molecular weights, mole fractions, and densities of pure 2-butanone and 2-propanol, 2-methyl-1-propanol, 2-butanol, 2-methyl-2-butanol, respectively. Dynamic viscosities η of binary mixtures of 2-butanone + 2-propanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-butanol at different temperatures were calculated by using densities and flow times by using the relation

$$\eta = K \cdot \rho(t - \mathrm{HC}) \quad (2)$$

where K is the viscometer constant (K = 0.01, as given by the manufacturer); ρ is density; and (t − HC) is the flow time adjusted by the Hagenbach correction factor and

$$\mathrm{HC} = E/Kt^2 \quad (3)$$

The value E/K = 70 500 is given in the instruction manual provided by the manufacturer.

Table 4. Densities ρ for 2-Butanone (1) + 2-Butanol (2) from T = (293.15 to 313.15) K

	ρ/g·cm^{-3}				
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
0.0000	0.80648	0.80235	0.79896	0.79418	0.79007
0.0684	0.80636	0.80216	0.79867	0.79388	0.78968
0.1365	0.80625	0.80198	0.79839	0.79358	0.78929
0.2044	0.80614	0.80179	0.79810	0.79328	0.78890
0.2721	0.80603	0.80161	0.79782	0.79298	0.78851
0.3395	0.80592	0.80143	0.79754	0.79268	0.78813
0.4066	0.80581	0.80125	0.79726	0.79239	0.78774
0.4735	0.80571	0.80107	0.79698	0.79209	0.78736
0.5402	0.80561	0.80090	0.79671	0.79180	0.78697
0.6066	0.80550	0.80072	0.79643	0.79151	0.78659
0.6727	0.80540	0.80055	0.79616	0.79122	0.78621
0.7387	0.80530	0.80038	0.79589	0.79093	0.78583
0.8044	0.80521	0.80010	0.79562	0.79064	0.78545
0.8698	0.80511	0.80004	0.79535	0.79035	0.78507
0.9350	0.80501	0.79987	0.79508	0.79006	0.78470
1.0000	0.80492	0.79970	0.79481	0.78978	0.78432

Table 5. Densities ρ for 2-Butanone (1) + 2-Methyl-2-Butanol (2) from T = (293.15 to 313.15) K

	ρ/g·cm^{-3}				
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
0.0000	0. 80961	0. 80501	0.80041	0.79581	0.79121
0.0803	0.80922	0.80457	0.79994	0.79530	0.79063
0.1583	0.80884	0.80415	0.79949	0.79482	0.79009
0.2341	0.80848	0.80374	0.79906	0.79436	0.78957
0.3077	0.80813	0.80335	0.79885	0.79392	0.78906
0.3794	0.80779	0.80297	0.79825	0.79349	0.78857
0.4490	0.80747	0.80260	0.79786	0.79307	0.78809
0.5168	0.80716	0.80224	0.79748	0.79267	0.78763
0.5828	0.80685	0.80189	0.79612	0.79227	0.78718
0.6471	0.80656	0.80156	0.79677	0.79189	0.78674
0.7097	0.80627	0.80123	0.79643	0.79152	0.78632
0.7707	0.80599	0.80091	0.79608	0.79115	0.78590
0.8302	0.80571	0.80060	0.79575	0.79079	0.78549
0.8882	0.80545	0.80029	0.79542	0.79044	0.78509
0.9448	0.80518	0.79999	0.79511	0.79010	0.78470
1.0000	0.80492	0.79970	0.79481	0.78978	0.78432

Discussion

Figure 1 shows the graphical variation of V^E for binary mixtures of 2-butanone with 2-propanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-butanol, from T = (293.15 to 313.15) K.

In the present study, the values of V^E are found to be positive for all the systems studied and at the said temperatures. But in the case of 2-butanone + 2-methyl-1-propanol, V^E values are found to be negative in initial stages up to 0.2 mol fractions and then positive, thus showing negative to positive trends in the values. For 2-butanone + 2-methyl-2-butanol, V^E increases with increasing temperatures. For all other systems, the values are decreased with increasing temperatures.

It is established that sign and magnitude of V^E give a good estimate of the unlike interactions in the binary mixtures. Generally, V^E can be considered as arising from three types of interaction between component molecules:

Physical interaction mainly consisting of dispersion forces or weak dipole−dipole interaction and making a positive contribution.[1−3]

Table 6. Viscosities η for 2-Butanone (1) + 2-Propanol (2) from T = (293.15 to 313.15) K

	η/mPa·s				
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
0.0000	2.2256	1.9102	1.7370	1.5242	1.3472
0.0595	1.8161	1.5957	1.4133	1.2715	1.1649
0.1282	1.5044	1.3616	1.2067	1.0948	1.0029
0.1724	1.2939	1.1845	1.0456	0.9637	0.8693
0.2326	1.1026	0.9992	0.9083	0.8366	0.7740
0.2941	0.9668	0.8812	0.8021	0.7488	0.6929
0.3572	0.8520	0.7675	0.7154	0.6663	0.6169
0.4217	0.7693	0.6949	0.6406	0.5987	0.5567
0.4878	0.7113	0.6289	0.5816	0.5428	0.4753
0.5556	0.6609	0.5801	0.5303	0.4834	0.4406
0.6250	0.6072	0.5071	0.4848	0.4314	0.3846
0.6962	0.5511	0.4516	0.4355	0.3751	0.3302
0.7693	0.5144	0.3852	0.3866	0.3345	0.3160
0.8442	0.4675	0.3530	0.3359	0.3060	0.2860
0.9211	0.4293	0.3262	0.2972	0.2758	0.2706
1.0000	0.3956	0.2828	0.2666	0.2601	0.2545

Table 7. Viscosities η for 2-Butanone (1) + 2-Methyl-1-propanol (2) from T = (293.15 to 313.15) K

	η/mPa·s				
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
0.0000	4.0366	3.3297	2.8752	2.4207	1.9666
0.0684	3.1376	2.6113	2.2402	1.9129	1.6255
0.1365	2.4294	2.0537	1.7799	1.5337	1.3300
0.2044	1.8623	1.5660	1.4042	1.1932	1.0736
0.2721	1.4260	1.2057	1.1041	0.9579	0.8538
0.3395	1.1106	0.9449	0.8637	0.7612	0.6894
0.4066	0.8561	0.7513	0.6760	0.6222	0.5674
0.4735	0.7002	0.6070	0.5418	0.5176	0.4600
0.5402	0.6142	0.5305	0.4663	0.4456	0.3948
0.6066	0.5380	0.4883	0.4135	0.4102	0.3400
0.6727	0.5271	0.4556	0.3743	0.3752	0.3138
0.7387	0.5071	0.4444	0.3713	0.3573	0.2909
0.8044	0.5079	0.4189	0.3607	0.3498	0.2754
0.8698	0.4996	0.4217	0.3443	0.3334	0.2800
0.9350	0.4722	0.3617	0.3135	0.3005	0.2769
1.0000	0.3956	0.2828	0.2666	0.2601	0.2545

Table 8. Viscosities η for 2-Butanone (1) + 2-Butanol (2) from T = (293.15 to 313.15) K

	η/mPa·s				
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
0.0000	3.6316	2.9975	2.4978	2.0542	1.7989
0.0684	2.9103	2.4289	2.0372	1.6915	1.4993
0.1365	2.3397	2.0069	1.6491	1.3391	1.2280
0.2044	1.8700	1.6125	1.3517	1.0543	1.0032
0.2721	1.4911	1.2989	1.0737	0.8161	0.8187
0.3395	1.1831	1.0509	0.8484	0.6282	0.6806
0.4066	0.9558	0.8537	0.6826	0.5076	0.5709
0.4735	0.7693	0.6870	0.5613	0.4126	0.4786
0.5402	0.6236	0.5600	0.4526	0.3601	0.4206
0.6066	0.5287	0.4800	0.3944	0.3260	0.3681
0.6727	0.4645	0.4282	0.3468	0.3051	0.3429
0.7387	0.4412	0.3922	0.3077	0.3090	0.3191
0.8044	0.4486	0.3620	0.3031	0.3112	0.2915
0.8698	0.4468	0.3482	0.3071	0.3186	0.2805
0.9350	0.4200	0.3000	0.2786	0.2966	0.2718
1.0000	0.3956	0.2828	0.2666	0.2601	0.2545

Chemical or specific interactions which include charge transfer, formation of hydrogen bonds, and other complex forming interactions resulting in negative contribution.

The structural contributions arising from geometrical fitting of one component into another due to difference in molar volumes resulting in negative V^E.

The positive V^E values in the present case are indicative of dispersion interaction between mixing components. This dispersion interaction may arise due to breaking of cohesive forces acting in like molecules with the subsequent increase[10] in V^E. Since normally dispersive interaction between unlike molecules is weaker than those between like molecules, it is reasonable that they contribute positively[10] to V^E. It appears that these two positive contributions largely overcome negative ones arising from the packing effect. Thus, addition of 2-butanone breaks weak dipole−dipole cohesive forces present in branched alcohols and vice versa with the subsequent increase in V^E.

Table 9. Viscosities η for 2-Butanone (1) + 2-Methyl-2-butanol (2) from T = (293.15 to 313.15) K

	η/mPa·s				
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
0.0000	5.1080	4.4740	3.9086	3.3871	2.9086
0.0803	3.8096	3.3500	2.9001	2.5207	2.2600
0.1583	2.8621	2.5206	2.1401	1.9050	1.7000
0.2341	2.1049	1.8500	1.5301	1.4208	1.2873
0.3077	1.5578	1.3700	1.0901	1.1034	0.9819
0.3794	1.1503	1.0541	0.8501	0.8400	0.7418
0.4490	0.8420	0.8221	0.6863	0.7188	0.5869
0.5168	0.6725	0.6579	0.5601	0.5865	0.4801
0.5828	0.5515	0.5913	0.5201	0.5202	0.4017
0.6471	0.4986	0.5219	0.5200	0.4801	0.3511
0.7097	0.4935	0.4894	0.4800	0.4507	0.3307
0.7707	0.4482	0.4437	0.4801	0.4505	0.3230
0.8302	0.4457	0.4344	0.4802	0.4503	0.3001
0.8882	0.4464	0.3813	0.4402	0.4012	0.2999
0.9448	0.4338	0.3142	0.3601	0.3200	0.2997
1.0000	0.3956	0.2828	0.2666	0.2601	0.2545

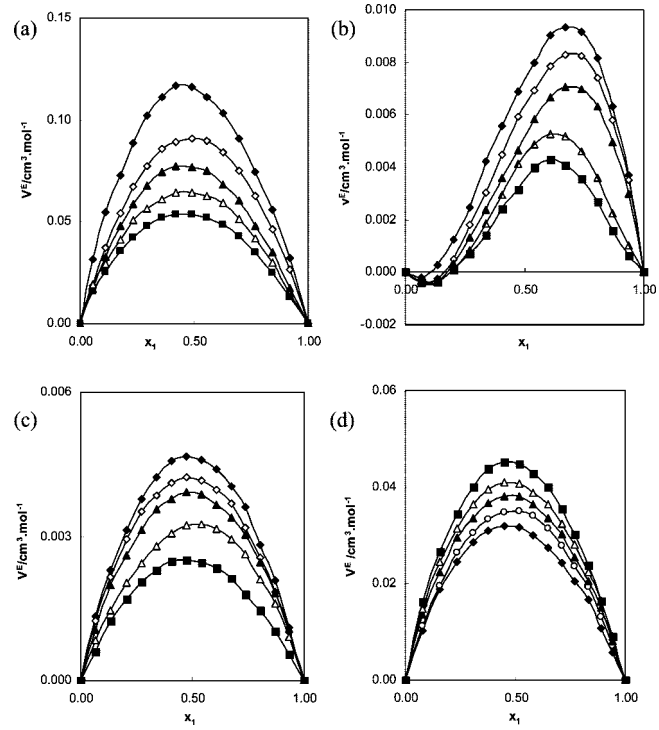

Figure 1. Excess molar volumes, V^E, for (a) 2-butanone (1) + 2-propanol (2), (b) 2-butanone (1) + 2-methyl-1-propanol (2), (c) 2-butanone (1) + 2-butanol (2), and (d) 2-butanone (1) + 2-methyl-2-butanol (2): ◆, 293.15 K; ◇, 298.15 K; ▲, 303.15 K; Δ, 308.15 K; ■, 313.15 K; solid curves calculated with the Redlich−Kister equation; symbols represents experimental values.

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