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Densities and excess molar volumes of alcohol + cyclohexylamine mixtures

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Abstract: Densities of binary mixtures of 1-propanol, or 2-butanol, or 1-pentanol + cyclohexylamine were measured at temperatures from 288.15 to 313.15 K and atmospheric pressure, while the densities for the system 2-methyl-2-propanol + cyclohexylamine were measured at temperatures from 303.15 to 323.15 K and atmospheric pressure. All measurements were performed using an Anton Paar DMA 5000 digital vibrating-tube densimeter. From the experimental densities, the excess molar volumes, V^E, were calculated.

Keywords: binary mixtures; densities; excess molar volumes; alcohols; cyclohexylamine.

INTRODUCTION

This study is a continuation of previous research dealing with the experimental determination or calculation of volumetric properties of binary and ternary mixtures containing different alcohols and aromatics, chlorinated aromatics or chlorinated alkanes.[1–6] The intention of this study was to provide a set of volumetric data in order to assess the influence of temperature, as well as the structure of the alcohol molecule (position of the OH group and alcohol chain length) in mixtures with cyclohexylamine on the molecular interactions between them.

Mixtures of alcohols and primary amines are an interesting class of systems exhibiting very strong negative deviations from the Raoult law. From a theoretical viewpoint, the volumetric properties of these mixtures are an important source of information for the characterization of the interactions between the components and they are also useful for understanding the liquid state theory. In addition, alcohols and amines are widely used in a variety of industrial and consumer applications and hence, knowledge of their physical properties is also of

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great importance from a practical point of view. Alcohols are in use as fuel, perfumes, cosmetics, paints, varnishes, drugs, explosives, fats, waxes, resins, plastics, rubber, detergents, *etc*.,[1–3] while cyclohexylamine is used in the production of pharmaceutical and other chemicals, including insecticides, pesticides, plasticizers, emulsifying agents, dyes, dry cleaning agents and corrosion inhibitors.[7]

In the present work, the densities, ρ, were measured for the following systems: 1-propanol, or 2-butanol, or 1-pentanol + cyclohexylamine at temperatures from 288.15 to 313.15 K and atmospheric pressure, and 2-methyl-2-propanol + cyclohexylamine at temperatures from 303.15 to 323.15 K and atmospheric pressure, since the melting point of 2-methyl-2-propanol is around 298 K. The excess molar volumes, V^E, of the investigated mixtures were calculated from the measured data.

Literature data of V^E values for the investigated systems cover a single temperature, 303.15 K.[8] In the hitherto published articles, no values of V^E were found covering the entire temperature range of the mixtures studied here.

For a complete insight into the behavior of alcohol + cyclohexylamine mixtures, the 1-butanol + cyclohexylamine system[9] was also included in the analysis.

EXPERIMENTAL

Materials

All products were of high purity (mass fraction purity > 0.99) and were used without further purification: 1-propanol > 0.995, 1-butanol > 0.995, 2-butanol > 0.99 and cyclohexylamine > 0.99 were supplied from Merck, while 2-methyl-2-propanol > 0.997 and 1-pentanol > > 0.99 were products from Fluka. All organic liquids were stored in brown glass bottles under an inert nitrogen atmosphere. The pure components were degassed in an ultrasonic bath immediately before sample preparation. The densities of the pure components together with the corresponding literature values[10-15] are listed in Table I.

TABLE I. Densities of the pure components

Substance	T / K	ρ / g·cm^{-3}	
		Experimental	Literature
1-Propanol	298.15	0.799692	0.79969[10], 0.79960[11]
2-Butanol	298.15	0.802528	0.8026[11], 0.80254[12]
2-Methyl-2-propanol	303.15	0.775412	0.77541[11], 0.77546[13]
1-Pentanol	298.15	0.810968	0.81090[11], 0.81096[14]
Cyclohexylamine	303.15	0.857671	0.85777[11], 0.85820[15]

Apparatus and procedure

The density measurements of the binaries (1-propanol, or 1-pentanol, or 2-butanol, or 2-methyl-2-propanol + cyclohexylamine) and the corresponding pure substances were realized using an Anton Paar DMA 5000 digital vibrating U-tube densimeter (with automatic viscosity correction) having an accuracy of $\pm 5\times10^{-6}$ g cm^{-3}. The temperature in the cell was controlled to ±0.001 K with a built-in solid-state thermostat. The temperature in the cell was measured by means of two integrated Pt 100 platinum thermometers and the temperature stability was

found to be better than ±0.002 K. The apparatus was calibrated daily using ambient air and ultra pure water. To minimize the errors in composition, all mixtures were prepared by mass using the cell and the procedure described previously.[16,17] A Mettler AG 204 balance with a precision of 1×10^{-4} g was used. The error in the calculation of the mole fraction was found to be less than $\pm1\times10^{-4}$. The experimental uncertainty in the density was less than $\pm1\times10^{-5}$ g cm^{-3}, while the average error in the excess molar volume was estimated to be better than $\pm3\times10^{-3}$ cm^{-3} mol^{-1}.

RESULTS AND DISCUSSION

The excess molar volumes, V^E, of binary mixtures were calculated from the density data by applying Eq. (1) (the values are given in Table II):

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

where x_1, x_2, M_1 and M_2 are the mole fraction and molar mass of components 1 and 2, respectively, while ρ, ρ_1 and ρ_2 are the measured densities of the mixture and the pure components 1 and 2, respectively.

TABLE II. Experimental densities, ρ, and excess molar volumes, V^E, for the alkanol (1) + cyclohexylamine (2) binary mixtures at different temperatures 288.15–323.15 K and atmospheric pressure

x_1	ρ / g·cm^{-3}	V^E / cm^3 mol^{-1}	x_1	ρ / g cm^{-3}	V^E / cm^3 mol^{-1}
1-Propanol (1) + cyclohexylamine (2)					
T = 288.15 K					
0.0000	0.871290	0.0000	0.6002	0.852683	–1.3633
0.0509	0.870750	–0.2073	0.7000	0.844776	–1.2147
0.1017	0.870088	–0.4014	0.7997	0.834754	–0.9312
0.1486	0.869388	–0.5726	0.8500	0.828866	–0.7418
0.1992	0.868514	–0.7466	0.8998	0.822459	–0.5250
0.3007	0.866227	–1.0467	0.9502	0.815368	–0.2770
0.4009	0.863037	–1.2608	1.0000	0.807690	0.0000
0.4998	0.858771	–1.3819			
T = 293.15 K					
0.0000	0.866747	0.0000	0.6002	0.848350	–1.3698
0.0509	0.866243	–0.2116	0.7000	0.840517	–1.2212
0.1017	0.865605	–0.4082	0.7997	0.830587	–0.9376
0.1486	0.864928	–0.5816	0.8500	0.824743	–0.7473
0.1992	0.864070	–0.7567	0.8998	0.818382	–0.5292
0.3007	0.861807	–1.0572	0.9502	0.811337	–0.2793
0.4009	0.858633	–1.2699	1.0000	0.803703	0.0000
0.4998	0.854393	–1.3896			
T = 298.15 K					
0.0000	0.862207	0.0000	0.6002	0.843999	–1.3757
0.0509	0.861732	–0.2152	0.7000	0.836238	–1.2273
0.1017	0.861122	–0.4150	0.7997	0.826395	–0.9434
0.1486	0.860461	–0.5899	0.8500	0.820597	–0.7524

TABLE II. Continued

x_1	ρ / g cm^{-3}	V^E / cm^3 mol^{-1}	x_1	ρ / g cm^{-3}	V^E / cm^3 mol^{-1}
1-Propanol (1) + cyclohexylamine (2)					
T = 298.15 K					
0.1992	0.859622	–0.7666	0.8998	0.814283	–0.5333
0.3007	0.857380	–1.0676	0.9502	0.807280	–0.2814
0.4009	0.854219	–1.2787	1.0000	0.799692	0.0000
0.4998	0.850004	–1.3959			
T = 303.15 K					
0.0000	0.857671	0.0000	0.6002	0.839630	–1.3812
0.0509	0.857223	–0.2188	0.7000	0.831934	–1.2327
0.1017	0.856634	–0.4211	0.7997	0.822178	–0.9490
0.1486	0.855990	–0.5978	0.8500	0.816427	–0.7576
0.1992	0.855164	–0.7756	0.8998	0.810149	–0.5366
0.3007	0.852939	–1.0769	0.9502	0.803196	–0.2837
0.4009	0.849790	–1.2867	1.0000	0.795650	0.0000
0.4998	0.845594	–1.4023			
T = 308.15 K					
0.0000	0.853138	0.0000	0.6002	0.835236	–1.3857
0.0509	0.852710	–0.2217	0.7000	0.827602	–1.2373
0.1017	0.852139	–0.4263	0.7997	0.817929	–0.9538
0.1486	0.851509	–0.6047	0.8500	0.812223	–0.7620
0.1992	0.850697	–0.7839	0.8998	0.805991	–0.5404
0.3007	0.848483	–1.0851	0.9502	0.799076	–0.2854
0.4009	0.845341	–1.2934	1.0000	0.791576	0.0000
0.4998	0.841161	–1.4076			
T = 313.15 K					
0.0000	0.848607	0.0000	0.6002	0.830816	–1.3894
0.0509	0.848196	–0.2244	0.7000	0.823240	–1.2410
0.1017	0.847641	–0.4313	0.7997	0.813647	–0.9579
0.1486	0.847020	–0.6109	0.8500	0.807982	–0.7657
0.1992	0.846216	–0.7910	0.8998	0.801787	–0.5427
0.3007	0.844011	–1.0924	0.9502	0.794911	–0.2860
0.4009	0.840874	–1.2993	1.0000	0.787466	0.0000
0.4998	0.836705	–1.4118			
1-Pentanol (1) + cyclohexylamine (2)					
T = 288.15 K					
0.0000	0.871290	0.0000	0.6003	0.848864	–1.1277
0.0506	0.870021	–0.1665	0.6998	0.842494	–0.9985
0.1001	0.868675	–0.3172	0.7962	0.835420	–0.7634
0.1500	0.867306	–0.4689	0.8500	0.831143	–0.5921
0.2002	0.865855	–0.6135	0.8995	0.827043	–0.4144
0.2997	0.862562	–0.8507	0.9501	0.822677	–0.2111
0.3995	0.858846	–1.0422	1.0000	0.818282	0.0000
0.5004	0.854296	–1.1412			

TABLE II. Continued

x_1	ρ / g cm^{-3}	V^E / cm^3 mol^{-1}	x_1	ρ / g cm^{-3}	V^E / cm^3 mol^{-1}
1-Pentanol (1) + cyclohexylamine (2)					
T = 293.15 K					
0.0000	0.866747	0.0000	0.6003	0.844821	–1.1339
0.0506	0.865544	–0.1710	0.6998	0.838550	–1.0045
0.1001	0.864254	–0.3248	0.7962	0.831578	–0.7691
0.1500	0.862936	–0.4789	0.8500	0.827355	–0.5968
0.2002	0.861531	–0.6251	0.8995	0.823304	–0.4180
0.2997	0.858315	–0.8631	0.9501	0.818988	–0.2135
0.3995	0.854658	–1.0524	1.0000	0.814635	0.0000
0.5004	0.850173	–1.1489			
T = 298.15 K					
0.0000	0.862207	0.0000	0.6003	0.840764	–1.1398
0.0506	0.861069	–0.1757	0.6998	0.834591	–1.0104
0.1001	0.859833	–0.3325	0.7962	0.827719	–0.7746
0.1500	0.858565	–0.4891	0.8500	0.823550	–0.6016
0.2002	0.857202	–0.6365	0.8995	0.819549	–0.4220
0.2997	0.854056	–0.8747	0.9501	0.815279	–0.2157
0.3995	0.850460	–1.0623	1.0000	0.810968	0.0000
0.5004	0.846039	–1.1565			
T = 303.15 K					
0.0000	0.857671	0.0000	0.6003	0.836693	–1.1456
0.0506	0.856593	–0.1799	0.6998	0.830615	–1.0161
0.1001	0.855410	–0.3400	0.7962	0.823839	–0.7799
0.1500	0.854186	–0.4984	0.8500	0.819726	–0.6065
0.2002	0.852868	–0.6477	0.8995	0.815771	–0.4256
0.2997	0.849789	–0.8860	0.9501	0.811547	–0.2178
0.3995	0.846251	–1.0719	1.0000	0.807278	0.0000
0.5004	0.841893	–1.1638			
T = 308.15 K					
0.0000	0.853138	0.0000	0.6003	0.832605	–1.1515
0.0506	0.852111	–0.1833	0.6998	0.826617	–1.0218
0.1001	0.850981	–0.3468	0.7962	0.819937	–0.7854
0.1500	0.849802	–0.5075	0.8500	0.815876	–0.6114
0.2002	0.848523	–0.6581	0.8995	0.811967	–0.4295
0.2997	0.845509	–0.8966	0.9501	0.807786	–0.2198
0.3995	0.842027	–1.0810	1.0000	0.803558	0.0000
0.5004	0.837730	–1.1709			
T = 313.15 K					
0.0000	0.848607	0.0000	0.6003	0.828501	–1.1569
0.0506	0.847630	–0.1867	0.6998	0.822595	–1.0262
0.1001	0.846545	–0.3528	0.7962	0.816008	–0.7896
0.1500	0.845407	–0.5155	0.8500	0.811997	–0.6148
0.2002	0.844167	–0.6675	0.8995	0.808133	–0.4319
0.2997	0.841215	–0.9063	0.9501	0.803997	–0.2208
0.3995	0.837791	–1.0896	1.0000	0.799817	0.0000
0.5004	0.833551	–1.1773			

TABLE II. Continued

x_1	ρ / g cm^{-3}	V^E / cm^3 mol^{-1}	x_1	ρ / g cm^{-3}	V^E / cm^3 mol^{-1}
2-Butanol (1) + cyclohexylamine (2)					
T = 288.15 K					
0.0000	0.871290	0.0000	0.5997	0.845367	–0.8520
0.0495	0.869943	–0.1407	0.7000	0.838111	–0.7422
0.1011	0.868364	–0.2692	0.7999	0.829857	–0.5521
0.1505	0.866768	–0.3858	0.8488	0.825461	–0.4333
0.1995	0.865069	–0.4914	0.8997	0.820714	–0.3012
0.3004	0.861240	–0.6829	0.9498	0.815822	–0.1579
0.3996	0.856833	–0.8145	1.0000	0.810689	0.0000
0.4974	0.851641	–0.8669			
T = 293.15 K					
0.0000	0.866747	0.0000	0.5997	0.841061	–0.8560
0.0495	0.865431	–0.1436	0.7000	0.833870	–0.7465
0.1011	0.863878	–0.2674	0.7999	0.825685	–0.5562
0.1505	0.862303	–0.3917	0.8488	0.821326	–0.4373
0.1995	0.860621	–0.4977	0.8997	0.816614	–0.3046
0.3004	0.856824	–0.6894	0.9498	0.811753	–0.1599
0.3996	0.852442	–0.8198	1.0000	0.806646	0.0000
0.4974	0.847283	–0.8710			
T = 298.15 K					
0.0000	0.862207	0.0000	0.5997	0.836727	–0.8617
0.0495	0.860918	–0.1464	0.7000	0.829591	–0.7524
0.1011	0.859388	–0.2722	0.7999	0.821468	–0.5619
0.1505	0.857832	–0.3978	0.8488	0.817137	–0.4423
0.1995	0.856164	–0.5044	0.8997	0.812454	–0.3087
0.3004	0.852393	–0.6966	0.9498	0.807614	–0.1621
0.3996	0.848033	–0.8261	1.0000	0.802528	0.0000
0.4974	0.842904	–0.8766			
T = 303.15 K					
0.0000	0.857671	0.0000	0.5997	0.832362	–0.8693
0.0495	0.856405	–0.1492	0.7000	0.825272	–0.7602
0.1011	0.854895	–0.2771	0.7999	0.817199	–0.5692
0.1505	0.853354	–0.4041	0.8488	0.812891	–0.4489
0.1995	0.851700	–0.5118	0.8997	0.808227	–0.3138
0.3004	0.847947	–0.7044	0.9498	0.803402	–0.1651
0.3996	0.843604	–0.8336	1.0000	0.798326	0.0000
0.4974	0.838501	–0.8840			
T = 308.15 K					
0.0000	0.853138	0.0000	0.5997	0.827960	–0.8790
0.0495	0.851889	–0.1518	0.7000	0.820909	–0.7704
0.1011	0.850393	–0.2816	0.7999	0.812872	–0.5785
0.1505	0.848866	–0.4106	0.8488	0.808580	–0.4572
0.1995	0.847222	–0.5194	0.8997	0.803926	–0.3201
0.3004	0.843483	–0.7132	0.9498	0.799109	–0.1690
0.3996	0.839155	–0.8429	1.0000	0.794030	0.0000
0.4974	0.834068	–0.8930			

TABLE II. Continued

x_1	ρ / g cm^{-3}	V^E / cm^3 mol^{-1}	x_1	ρ / g cm^{-3}	V^E / cm^3 mol^{-1}
2-Butanol (1) + cyclohexylamine (2)					
T = 313.15 K					
0.0000	0.848607	0.0000	0.5997	0.823519	–0.8912
0.0495	0.847368	–0.1542	0.7000	0.816495	–0.7829
0.1011	0.845885	–0.2864	0.7999	0.808484	–0.5902
0.1505	0.844366	–0.4171	0.8488	0.804198	–0.4673
0.1995	0.842729	–0.5274	0.8997	0.799548	–0.3281
0.3004	0.838998	–0.7227	0.9498	0.794725	–0.1736
0.3996	0.834678	–0.8534	1.0000	0.789632	0.0000
0.4974	0.829603	–0.9040			
2-Methyl-2-propanol (1) + cyclohexylamine (2)					
T = 303.15 K					
0.0000	0.857671	0.0000	0.5998	0.820236	–1.0212
0.0508	0.855457	–0.1703	0.6997	0.810864	–0.9197
0.1002	0.853151	–0.3215	0.7999	0.800285	–0.7173
0.1502	0.850673	–0.4619	0.8712	0.792153	–0.5281
0.2001	0.848023	–0.5854	0.8992	0.788654	–0.4232
0.3005	0.842301	–0.8051	0.9504	0.782167	–0.2309
0.3991	0.835940	–0.9560	1.0000	0.775412	0.0000
0.4996	0.828512	–1.0243			
T = 308.15 K					
0.0000	0.853138	0.0000	0.5998	0.815570	–1.0686
0.0508	0.850919	–0.1761	0.6997	0.806147	–0.9683
0.1002	0.848606	–0.3324	0.7999	0.795480	–0.7610
0.1502	0.846119	–0.4776	0.8712	0.787246	–0.5629
0.2001	0.843460	–0.6058	0.8992	0.783692	–0.4522
0.3005	0.837714	–0.8337	0.9504	0.777091	–0.2476
0.3991	0.831325	–0.9915	1.0000	0.770193	0.0000
0.4996	0.823876	–1.0668			
T = 313.15 K					
0.0000	0.848607	0.0000	0.5998	0.810845	–1.1164
0.0508	0.846376	–0.1816	0.6997	0.801362	–1.0173
0.1002	0.844050	–0.3430	0.7999	0.790593	–0.8046
0.1502	0.841553	–0.4936	0.8712	0.782252	–0.5976
0.2001	0.838878	–0.6262	0.8992	0.778642	–0.4811
0.3005	0.833102	–0.8630	0.9504	0.771925	–0.2642
0.3991	0.826681	–1.0284	1.0000	0.764884	0.0000
0.4996	0.819193	–1.1098			
T = 318.15 K					
0.0000	0.844073	0.0000	0.5998	0.806063	–1.1649
0.0508	0.841824	–0.1869	0.6997	0.796506	–1.0665
0.1002	0.839485	–0.3541	0.7999	0.785624	–0.8479
0.1502	0.836970	–0.5096	0.8712	0.777167	–0.6313
0.2001	0.834276	–0.6469	0.8992	0.773501	–0.5092

TABLE II. Continued

x_1	ρ / g cm^{-3}	V^E / cm^3 mol^{-1}	x_1	ρ / g cm^{-3}	V^E / cm^3 mol^{-1}
2-Methyl-2-propanol (1) + cyclohexylamine (2)					
T = 318.15 K					
0.3005	0.828457	–0.8922	0.9504	0.766665	–0.2799
0.3991	0.821996	–1.0656	1.0000	0.759488	0.0000
0.4996	0.814465	–1.1538			
T = 323.15 K					
0.0000	0.839547	0.0000	0.5998	0.801219	–1.2122
0.0508	0.837268	–0.1913	0.6997	0.791580	–1.1145
0.1002	0.834906	–0.3635	0.7999	0.780572	–0.8893
0.1502	0.832370	–0.5243	0.8712	0.771995	–0.6632
0.2001	0.829655	–0.6667	0.8992	0.768268	–0.5351
0.3005	0.823784	–0.9207	0.9504	0.761320	–0.2944
0.3991	0.817275	–1.1023	1.0000	0.754015	0.0000
0.4996	0.809685	–1.1965			

The obtained V^E values were fitted to a modified Redlich–Kister (RK) polynomial,[18] whereby the degree of polynomial expansion, m, was determined by means of the F-test:[19]

$$V^E = x_1 x_2 \sum_{p=0}^{m} B_p (x_1 - x_2)^p \tag{2}$$

where B_p denotes the temperature dependent parameter:

$$B_p = \sum_{q=0}^{k} B_{pq} T^q \tag{3}$$

where T is the absolute temperature. Additional analysis showed that the optimal number of parameters k was 3, because any further increase in the number of parameters did not result in an improvement of the fit quality.

The results were also fitted and explained using the reduced excess molar volume, $V^E/x_1(1 - x_1)$, which has a better physical significance and is more sensitive than V^E to interactions which occur in dilute regions.[20]

$$\frac{V^E}{x_1(1-x_1)} = \sum_{n=0}^{1} A_n x^n = A_0 + A_1 x_1 + A_2 x_1^2 \tag{4}$$

where the optimal number of parameters A_n was 3.

The unique sets of adjustable parameters B_{pq} over whole temperature range and adjustable parameters A_n of Eq. (4) at each temperature for the investigated binary systems, and the corresponding root mean square deviations defined by the equation:

$$\sigma = \sqrt{\sum_{i=1}^{N} \frac{(Y_{\mathrm{exp},i}^{\mathrm{E}} - Y_{\mathrm{cal},i}^{\mathrm{E}})^2}{N}} \quad (5)$$

are given in Table III and Table IV, respectively. In Eq. (5), Y stands for V^{E} and $V^{\mathrm{E}}/x_1(1 - x_1)$, while N denotes the number of experimental data points.

TABLE III. Fitting parameters, B_{pq}, of Eq. (3) and the root mean square deviation, σ/ cm^3 mol^{-1}

1-Propanol (1) + cyclohexylamine (2)				
288.15–313.15 K	B_{00} = 2.9470	B_{01} = –0.0515	B_{02} = 7.7×10^{-5}	σ = 0.0030
	B_{10} = –4.9954	B_{11} = 0.0217	B_{12} = –2.8×10^{-5}	
	B_{20} = 4.7076	B_{21} = –0.0184	B_{23} = 1.5×10^{-5}	
	B_{30} = 1.9405	B_{31} = –0.0086	B_{32} = 1.0×10^{-5}	
1-Butanol(1) + cyclohexylamine (2)				
288.15–313.15 K	B_{00} = –0.6285	B_{01} = –0.0244	B_{02} = 3.2×10^{-5}	σ = 0.0050
	B_{10} = 2.5151	B_{11} = –0.0282	B_{12} = 5.6×10^{-5}	
	B_{20} = 9.6774	B_{21} = –0.0518	B_{23} = 7.2×10^{-5}	
	B_{30} = –17.7455	B_{31} = 0.1229	B_{32} = –2.1×10^{-4}	
1-Pentanol (1) + cyclohexylamine (2)				
288.15–313.15 K	B_{00} = –2.9435	B_{01} = –0.0051	B_{02} = –0.2×10^{-5}	σ = 0.0025
	B_{10} = –6.7427	B_{11} = 0.0322	B_{12} = –4.2×10^{-5}	
	B_{20} = 19.1794	B_{21} = –0.1133	B_{23} = 1.7×10^{-4}	
	B_{30} = 3.6921	B_{31} = –0.0184	B_{32} = 2.5×10^{-5}	
2-Butanol (1) + cyclohexylamine (2)				
288.15–313.15 K	B_{00} = –12.2075	B_{01} = 0.0638	B_{02} = –1.2×10^{-4}	σ = 0.0033
	B_{10} = –10.2348	B_{11} = 0.0656	B_{12} = –1.1×10^{-4}	
	B_{20} = –6.7604	B_{21} = 0.0558	B_{23} = –1.1×10^{-4}	
	B_{30} = –0.0725	B_{31} = 0.0039	B_{32} = –1.0×10^{-5}	
2-Methyl-2-propanol (1) + cyclohexylamine (2)				
288.15–313.15 K	B_{00} = 2.8491	B_{01} = –0.0119	B_{02} = – 3.6×10^{-5}	σ = 0.0042
	B_{10} = 8.1933	B_{11} = –0.0350	B_{12} = 1.9×10^{-5}	
	B_{20} = 31.3276	B_{21} = –0.1879	B_{23} = 2.8×10^{-4}	
	B_{30} = 10.4360	B_{31} = –0.0654	B_{32} = 1.0×10^{-4}	

The results of ρ and V^{E} for the investigated binaries, in the investigated temperature range and over the entire concentration range, are summarized in Table II, while Fig. 1 shows the dependence $V^{\mathrm{E}} - x_1$ for all systems measured in this work and for 1-butanol + cyclohexylamine[9] at the temperature 303.15 K. The symbols in Fig. 1 present the experimental V^{E} values, while the solid lines refer to the values calculated from the modified Redlich–Kister equation using the B_{pq} parameters given in Table III.

The ρ and V^{E} data taken from literature for the systems studied cover only 303.15 K.[8] For the 1-pentanol + cyclohexylamine binary system, the agreement between the presented and the literature values is very good, while the experimental points of Dharmaraju *et al.*[8] obtained at 303.15 K for the systems con-

taining 1-propanol, or 2-butanol, or 2-methyl-2-propanol and cyclohexylamine are somewhat higher. In minimum region, at equimolar composition, the discrepancy between the present determined and the literature values is about 10 % for 1-propanol, or 2-methyl-2-propanol + cyclohexylamine, and 15 % for the 2-butanol + cyclohexylamine system.

TABLE IV. Fitting parameters, A_n, of Eq. (4) and root mean square deviation, σ

T / K	A_0	A_1	A_2	σ / cm^3 mol^{-1}
1-Propanol (1) + cyclohexylamine (2)				
288.15	–4.0167	–4.0083	2.1905	0.0394
293.15	–4.1111	–3.8102	2.0319	0.0384
298.15	–4.2023	–3.6064	1.8660	0.0350
303.15	–4.2896	–3.4024	1.6961	0.0334
308.15	–4.3637	–3.2313	1.5528	0.0302
313.15	–4.4289	–3.0968	1.4569	0.0285
1-Butanol(1) + cyclohexylamine (2)[a]				
288.15	–3.6363	–3.7635	2.2793	0.0744
293.15	–3.7373	–3.5188	2.0767	0.0745
298.15	–3.8246	–3.3350	1.9444	0.0717
303.15	–3.9118	–3.1409	1.7990	0.0703
308.15	–3.9889	–2.9728	1.6721	0.0678
313.15	–4.0544	–2.8346	1.5640	0.0654
1-Pentanol (1) + cyclohexylamine (2)				
288.15	–3.1369	–4.2954	2.9793	0.0593
293.15	–3.2460	–4.0521	2.7925	0.0566
298.15	–3.3586	–3.7894	2.5880	0.0554
303.15	–3.4627	–3.5553	2.4074	0.0534
308.15	–3.5537	3.3630	2.2572	0.0502
313.15	–3.6354	–3.2083	2.1564	0.0498
2-Butanol (1) + cyclohexylamine (2)				
288.15	–2.7800	–2.2347	1.7603	0.0488
293.15	–2.8223	–2.1408	1.6646	0.0513
298.15	–2.8903	–1.9786	1.5148	0.0508
303.15	–2.9587	–1.8253	1.3591	0.0501
308.15	–3.0222	–1.7012	1.2114	0.0491
313.15	–3.0831	–1.5993	1.0655	0.0472
2-Methyl-2-propanol (1) + cyclohexylamine (2)				
303.15	–3.4535	–1.1049	–0.3463	0.0396
308.15	–3.5752	–1.0557	–0.6481	0.0411
313.15	–3.6922	–1.0383	–0.9189	0.0431
308.15	–3.8057	–1.0598	–1.1377	0.0432
323.15	–3.9089	–1.1000	–1.3263	0.0427

[a]Parameters obtained for the experimental data already presented in the literature[9]

The experimental $V^E/x_1(1 - x_1)$ values and those calculated by Eq. (4) at 303.15 K are plotted in Fig. 2 as a function of the mole fraction of an alcohol.

The non-linear curves obtained for all investigated systems clearly show their non-ideal behavior.

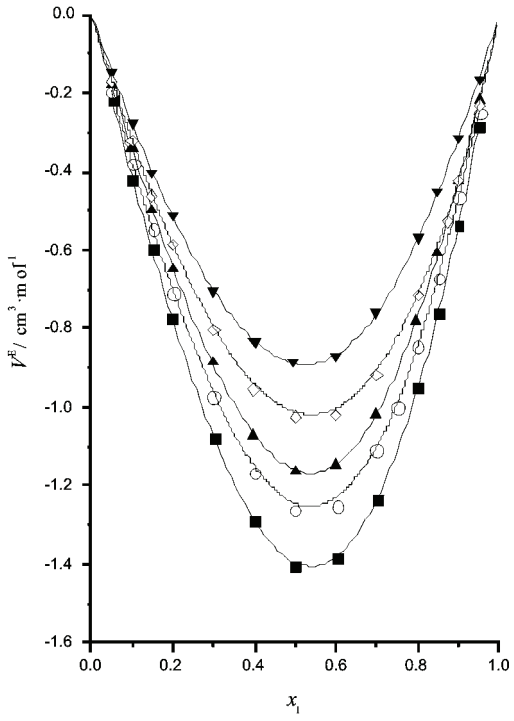

Fig. 1. Experimental values of V^E at 303.15 K for the systems: (■) 1-propanol (1) + + cyclohexylamine (2); (○) 1-butanol (1) + + cyclohexylamine (2);[9] (▲) 1-pentanol (1) + cyclohexylamine (2); (▼) 2-butanol (1) + cyclohexylamine (2); (◇) 2-methyl--2-propanol (1) + cyclohexylamine (2). The symbols refer to the experimental points, while the lines present the results calculated using Eq. (2) with the parameters presented in Table III.

The magnitude and the sign of V^E can arise from two opposing factors:[21] (*i*) the positive contribution is a consequence of the disruption of the hydrogen bonds in the self-associated alcohol and the dipole–dipole interactions between alcohol monomer and multimer. The self-association of the amine molecules is rather small; (*ii*) negative contributions arise from strong intermolecular interactions attributed to charge-transfer, dipole–dipole interactions and hydrogen bonding between unlike molecules. Hence, the negative V^E values of the investigated systems assume that heteroassociates forming cross complexes in the alcohol + amine mixtures have stronger O–H···N bonds than O–H···O and N––H···N bonds. This can be explained qualitatively by the fact that the free electron pair around the N atoms with less *s* and more *p* character has a higher polarizability and acts as a good proton acceptor for the donor –OH groups of the alcohols, which are more efficient than the –OH group itself. The negative sign of V^E indicates a net packing effect contributed to by structural changes arising from interstitial accommodation. As can be seen from Fig. 1, the negative V^E values are larger in the mixture with 1-propanol and decrease as the chain length of the 1-alkanol increases. This trend indicates that the strength of the intermolecu-

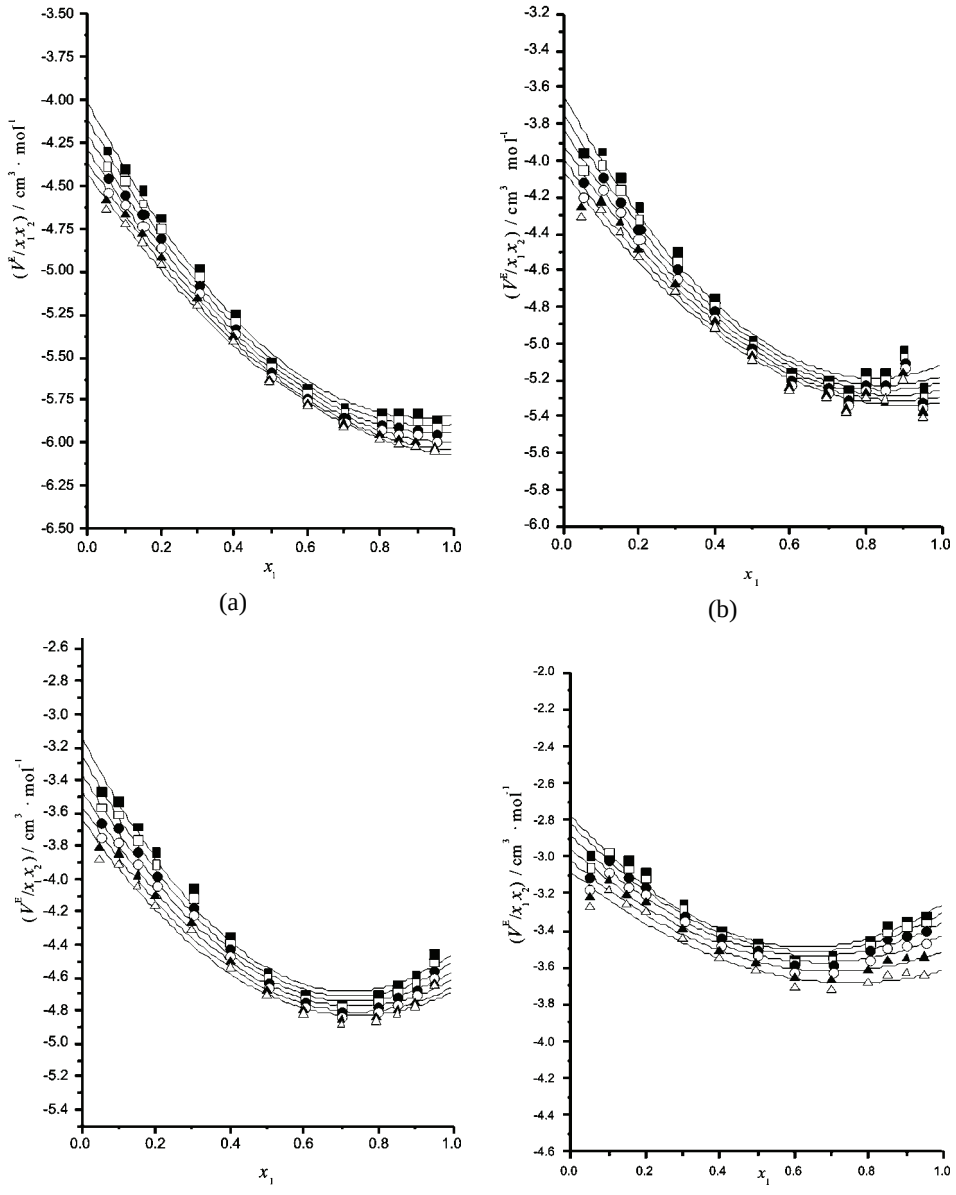

Fig. 2. Values of $V^E/x_1(1-x_1)$ data at (■) 288.15, (□) 293.15 K, (●) 298.15 K, (○) 303.15 K, (▲) 308.15 K, (Δ) 313.15 K, (◆) 318.15 K and (◇) 323.15 K for the systems: (a) 1-propanol (1) + cyclohexylamine (2); (b) 1-butanol (1) + cyclohexylamine (2);[9] (c) 1-pentanol (1) + cyclohexylamine (2); (d) 2-butanol (1) + cyclohexylamine (2). The symbols refer to the experimental points, while the lines present the results calculated using Eq. (4) with the parameters presented in Table IV.

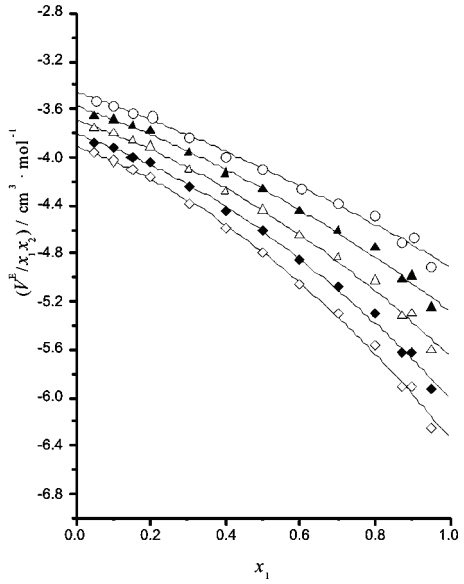

Fig. 2e. Values of $V^E/x_1(1 - x_1)$ data at (■) 288.15, (□) 293.15 K, (●) 298.15 K, (○) 303.15 K, (▲) 308.15 K, (Δ) 313.15 K, (◆) 318.15 K and (◇) 323.15 K for the system 2-methyl-2-propanol (1) + cyclohexylamine (2). The symbols refer to the experimental points, while the lines present the results calculated using Eq. (4) with the parameters presented in Table IV.

lar hydrogen bonding of cyclohexylamine with 1-propanol is much stronger than with the other higher 1-alcohols in the following order: 1-propanol > 1-butanol > 1-pentanol. These strengths of the interaction OH···NH_2 bonds suggest that the proton donating ability of 1-alcohols is of the same order. Namely, longer 1-alcohols would increase the basicity of the oxygen and make the hydroxyl proton less available for H bonding. In addition, it means that the most efficient packing can be attributed to the lower alcohol, which decreases with increasing chain length of 1-alcohol, where the packing effects are the result of their lower self-association (higher breaking of their H bonds) and the fact that the crowded molecules of amine, as a consequence of steric hindrance, are better packed in the more open structure of the longer alcohols. Also, the effect of increasing chain length of the 1-alcohol for a given amine can be considered using the effective dipole moment. Bearing in mind the discussions given in previous works referring to 1-alcohols and various amines, it can be concluded that in the present systems the following behavior could be expected. In the systems of 1-alcohols with cyclohexylamine, the absolute value of the V^E decreases with decreasing effective dipole moment of the alcohol.

The trend in the negative values of V^E for mixtures of cyclohexylamine with branched alcohols (2-butanol, 2-methyl-2-propanol) (Table II) compared to 1-butanol[9] is in the order: 1-butanol > 2-methyl-2-propanol > 2-butanol, suggesting that the interactions between tertiary alcohol and cyclohexylamine are stronger than between the secondary alcohol with cyclohexylamine, which in turn are stronger than the interactions between the primary alcohol and the amine.[8] The

results shown in Fig. 1 indicate that V^E of the mixture with 2-methyl-2-propanol are more negative than those with 2-butanol. Qualitatively, this could be explained by the fact that the oxygen atom of 2-methyl-2-propanol should be regarded as a better acceptor towards the NH proton of the amine than the oxygen atoms of the 2-butanol. Also, the system with 2-methyl-2-propanol suggests that the steric hindrance of the *tert*-butyl group tends to hamper the complex less than with 2-butanol. This is a consequence of a predominating electrometric effect (+I effect) over steric effect in 2-methyl-2-propanol.[8,22]

The influence of temperature on the V^E for the systems containing 1-propanol, or 1-butanol,[9] or 1-pentanol, or 2-butanol is almost negligible and the V^E values become only slightly more negative with increasing temperature. Only in the case of 2-methyl-2-propanol system was the influence of temperature more expressed. These facts can possibly be explained as a balance of two opposing effects caused by an increase in the kinetic energy of the different molecules: (*i*) the association constants of mixed complexes decrease with increasing temperature and the OH–N interactions decrease, (*ii*) the number of species increases after breakage of the complexes and (*iii*) the interstitial accommodation of one molecule into the other is facilitated. Thus, the effects (*i*) give an increase of V^E, while the effects (*ii*) and (*iii*) cause a decrease of V^E.

CONCLUSIONS

The densities of the binary mixtures (1-propanol, or 1-pentanol, or 2-butanol, or 2-methyl-2-propanol + cyclohexylamine) were measured in the temperature range 288.15–323.15 K at atmospheric pressure and the excess molar volumes V^E were calculated.

For all the investigated binary systems and the system with 1-butanol,[9] the negative values of V^E for the mixtures of cyclohexylamine with 1-alcohols lie in the order 1-propanol>1-butanol>1-pentanol. The value of V^E absolutely decreases when the chain length of the 1-alcohol molecules increases. The negative values of V^E in the mixtures of the same amine with branched alcohols compared to 1-butanol[9] are in the order: 1-butanol > 2-methyl-2-propanol > 2-butanol, suggesting that the interactions of tertiary alcohols are stronger than those of secondary alcohols in mixtures with cyclohexylamine. It is clear that the magnitude of V^E depends on the chain length of the alcohol and position of hydroxyl group in the alcohol molecule.

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ИЗВОД

ГУСТИНЕ И ДОПУНСКЕ МОЛАРНЕ ЗАПРЕМИНЕ СМЕША АЛКОХОЛ + ЦИКЛОХЕКСИЛАМИН

ИВОНА Р. РАДОВИЋ, МИРЈАНА Љ. КИЈЕВЧАНИН, АЛЕКСАНДАР Ж. ТАСИЋ, БОЈАН Д. ЂОРЂЕВИЋ и СЛОБОДАН П. ШЕРБАНОВИЋ

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Густине бинарних смеша (1-пропанол или 2-бутанол или 1-пентанол + циклохексиламин) су мерене у температурном интервалу 288,15–313,15 K и на атмосферском притиску, а густине система 2-метил-2-пропанол + циклохексиламин су мерене у температурном интервалу 303,15–323,15 K и на атмосферском притиску. Сва мерења су извршена на Anton Paar DMA 5000 дигиталном густиномеру. Из експерименталних вредности густина израчунате су допунске моларне запремине наведених смеша.

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