Density and Excess Molar Volume for Binary Mixtures of Naphthenic Acid Ionic Liquids and Ethanol

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The design and synthesis of biodegradable ionic liquids has been one of the ways to accelerate the pace of ionic liquid large-scale industrial applications and prevent environmental hazards. The knowledge of thermodynamic properties for the mixtures of biodegradable ionic liquids with organic solvent or water has been paramount for the design of many technological processes. In this work, the densities of two binary systems for biodegradable naphthenic acid ionic liquids, choline cyclohexane carboxylate ([Ch][CHC]), and choline cyclopentane carboxylate ([Ch][CPC]) with ethanol were measured over the whole range of compositions from (293.15 to 323.15) K. The excess molar volumes of two systems were obtained from experimental data and fitted to the Redlich−Kister equation. The results showed that V^E values were negative over the entire composition range, and its absolute values increased slightly with increasing temperature from (293.15 to 323.15) K. A minimum value of the two systems was located at 0.3 and 0.4, respectively. Estimated coefficients and standard error value were also presented.

Introduction

In recent years, room-temperature ionic liquids (RTILs) are showing more and more promising perspectives in the diverse fields of organic synthesis,[1] catalysis or biocatalysis,[2−6] materials science,[7] electrochemistry,[8] and separation technology[9−12] due to their unique physicochemical properties at the laboratory level and even on the industrial scale.[13,14] With the development of the industrialization process of RTILs, more and more researchers pay attention to the life cycle analysis of RTILs,[15] and some environmental factors were considered. One of them is the biodegradability of RTILs because biodegradation is a main process for removal of chemicals from the environment, and the biodegradability investigation of RTILs complies with the 10th of the 12 Green Chemistry principles.[16] Several studies[17−23] had already focused on design and synthesis of biodegradable RTILs. We also investigated the biodegradability of RTILs, and ten biodegradable naphthenic acid ionic liquids (NAILs) were prepared with choline and naphthenic acids as raw materials.[24]

The thermodynamic properties of the mixtures of ionic liquids with organic molecular liquids are paramount for the design of many technological processes, especially volumetric property, and this property of RTILs was most investigated, for example, binary mixtures containing imidazole,[25−27] pyridinium,[28] etc. However, the data on volumetric properties of new task-specific ionic liquids are rather limited.

To improve the biodegradability of ionic liquids, it is necessary for us to understand their structure and properties relationships. So we chose two biodegradable NAILs, choline cyclohexane carboxylate ([Ch][CHC]) and choline cyclopentane carboxylate ([Ch][CPC]), and their structures were shown in Scheme 1. The corresponding binary mixtures containing the two kinds of ionic liquids and ethanol were prepared. The densities of two binary systems were measured over the whole range of compositions from (293.15 to 323.15) K at atmospheric pressure. The excess molar volume of these two binary systems was investigated and fitted to the Redlich−Kister equation. The effects of ethanol content and temperature on the association behavior were analyzed.

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Experimental Section

Materials. Ethanol was supplied by Sinopharm Chemical Reagent Beijing Co., Ltd. with mass fraction > 0.999. [Ch][CHC] and [Ch][CPC] were prepared by the neutralization method from a single, one-pot reaction (see Scheme 2), which is the same as our previous work,[24] and its water content was determined to be about 300 ppm by Karl Fischer titration (751 GPD Titrino, Metrohm, Switzerland).

Apparatus and Procedure. The mixtures of NAILs and ethanol were prepared by mass using a BS124S electronic digital balance accurate to within ± 0.1 mg. The uncertainty in the mole fraction of the mixtures was estimated to less than ± 0.0001.

The densities of the pure compounds and their mixtures were measured by the Anton Paar DMA 5000 vibrating-tube densimeter with an uncertainty of $1 \cdot 10^{-6}$ g·cm^{-3} and accuracy of $\pm 5 \cdot 10^{-6}$ g·cm^{-3}. Two integrated Pt 100 platinum thermometers provided good precision in temperature readings ($\delta T = \pm 0.001$ K). The detailed measuring step was the same as in our previous work.[29] The experimental and literature data of NAILs and ethanol at several temperatures were given in Table 1. The relative error of four densities for NAILs between this work and our previous work[24] was calculated, and the results were 0.31 %, 0.20 %, 0.16 %, and 0.08 %, respectively. The average relative error was 0.19 % and less than 0.3 %. The overall average relative error of densities for ethanol was 0.036 %. The above results show that our experimental data were in good agreement with literature data.

Results and Discussion

The densities of binary system for NAILs (1) + ethanol (2) over the temperature range from (293.15 to 323.15) K were

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Scheme 1. Molecular Structures of [Ch][CHC] and [Ch][CPC]

[Ch][CHC] [Ch][CPC]

Scheme 2. Synthesis of NAILs

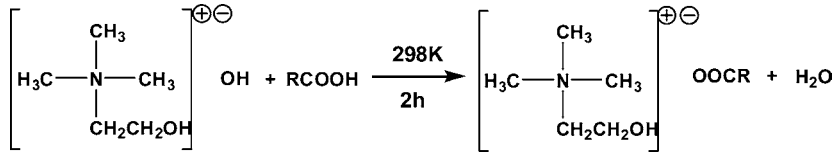

Table 1. Comparison of Measured Densities ρ and Molar Volume of [Ch][CHC], [Ch][CPC], and Ethanol with Literature Values

	[Ch][CHC]				[Ch][CPC]				ethanol			
	ρ/g·cm^{-3}				ρ/g·cm^{-3}				ρ/g·cm^{-3}			
T/K	exptl	lit.	$100\Delta\rho/\rho$	V_m/cm^3·mol^{-1}	exptl	lit.	$100\Delta\rho/\rho$	V_m/cm^3·mol^{-1}	exptl	lit.	$100\Delta\rho/\rho$	V_m/cm^3·mol^{-1}
293.15	1.070688			215.75	1.092476			198.63	0.789921	0.7897[30]	0.03	58.32
298.15	1.067771	1.064432[24]	0.31	216.34	1.089616	1.087904[24]	0.16	199.15	0.785631	0.7853[30]	0.04	58.64
										0.78522[31]	0.05	
303.15	1.064857			216.93	1.086760			199.68	0.781313	0.7809[30]	0.04	58.96
308.15	1.061954			217.52	1.083909			200.20	0.776961	0.7765[30]	0.06	59.30
313.15	1.059052	1.061194[24]	0.20	218.12	1.081066	1.081890[24]	0.08	200.73	0.772569	0.7723[30]	0.03	59.63
318.15	1.056156			218.72	1.078224			201.26	0.768129	0.7679[30]	0.02	59.98
323.15	1.053262			219.32	1.075387			201.79	0.763643	0.7635[30]	0.02	60.33

presented in Table 2. It could be readily observed that the densities decreased with the increase of ethanol content or temperature, which approached to that of ethanol.

The excess molar volumes (V^E) were calculated from the experimental data by eq 1[32,33]

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

where ρ was density of mixtures; x_1 and x_2 were mole fractions; M_1 and M_2 were molar masses; and ρ_1 and ρ_2 were densities of NAILs (1) and ethanol (2), respectively. All values of excess molar volume were fitted to the Redlich−Kister polynomial eq 2[32,33]

$$V^E = x_1(1 - x_1)\sum_{i=0}^{k} A_i(2x_1 - 1)^i \quad (2)$$

where A_i were adjustable parameters. The standard derivation σ was correlated by eq 3

$$\sigma = \left[\frac{\sum (V^E_{exp} - V^E_{cal})^2}{n - p}\right]^{1/2} \quad (3)$$

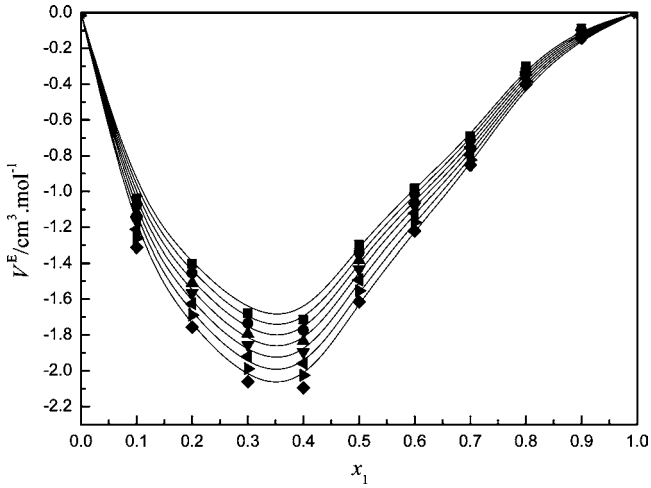

Figure 1. Excess molar volume V^E vs mole fraction x of [Ch][CHC] for [Ch][CHC] (1) + ethanol (2): ■, 293.15 K; ●, 298.15 K; ▲, 303.15 K; ▼, 308.15 K; solid triangle pointing left, 313.15 K; solid triangle pointing right, 318.15 K; ◆, 323.15 K. The solid curves are calculated with the Redlich−Kister equation, and the symbols represent experimental values.

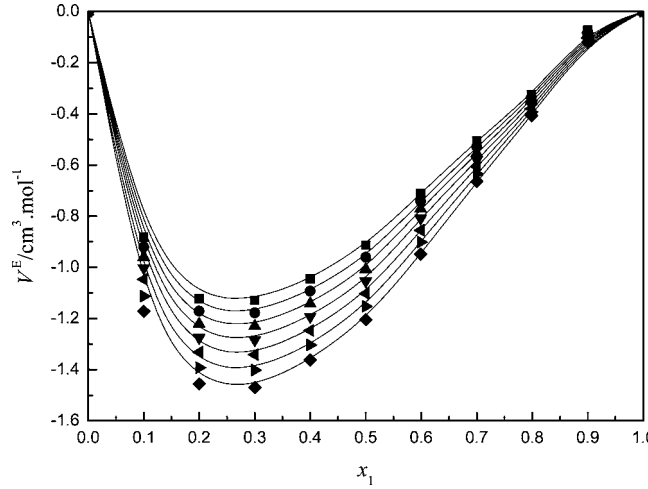

Figure 2. Excess molar volume V^E vs mole fraction x of [Ch][CPC] for [Ch][CPC] (1) + ethanol (2): ■, 293.15 K; ●, 298.15 K; ▲, 303.15 K; ▼, 308.15 K; solid triangle pointing left, 313.15 K; solid triangle pointing right, 318.15 K; ◆, 323.15 K. The solid curves are calculated with the Redlich−Kister equation, and the symbols represent experimental values.

Table 2. Experimental Densities ρ and Excess Molar Volume V^E for Binary Mixtures of [Ch][CHC] (1) + Ethanol (2) and [Ch][CPC] (1) + Ethanol (2)

x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15
				[Ch][CHC] (1) + Ethanol (2)			
				ρ/g·cm^{-3}			
0.0000	0.789921	0.785631	0.781313	0.776961	0.772569	0.768129	0.763643
0.1000	0.884111	0.880427	0.876732	0.873026	0.869305	0.865569	0.861812
0.2000	0.939492	0.936092	0.932694	0.929294	0.925891	0.922481	0.919065
0.3000	0.977638	0.974422	0.971201	0.967983	0.964764	0.961547	0.958330
0.4000	1.003876	1.000800	0.997714	0.994621	0.991526	0.988431	0.985334
0.5000	1.020607	1.017520	1.014426	1.011378	1.008388	1.005380	1.002364
0.5999	1.034454	1.031406	1.028358	1.025304	1.022278	1.019320	1.016343
0.7000	1.045820	1.042819	1.039825	1.036831	1.033834	1.030832	1.027835
0.8000	1.054632	1.051664	1.048699	1.045742	1.042782	1.039815	1.036855
0.8999	1.062969	1.060028	1.057095	1.054166	1.051243	1.048324	1.045406
1.0000	1.070688	1.067771	1.064857	1.061954	1.059052	1.056156	1.053262
				V^E/cm^3·mol^{-1}			
0.1000	–1.0391	–1.0791	–1.1209	–1.1648	–1.2113	–1.2607	–1.3128
0.2000	–1.4024	–1.4540	–1.5084	–1.5654	–1.6258	–1.6896	–1.7570
0.3000	–1.6786	–1.7355	–1.7943	–1.8558	–1.9206	–1.9891	–2.0615
0.4000	–1.7145	–1.7738	–1.8341	–1.8953	–1.9592	–2.0262	–2.0963
0.5000	–1.2979	–1.3400	–1.3828	–1.4329	–1.4933	–1.5536	–1.6157
0.5999	–0.9826	–1.0150	–1.0487	–1.0818	–1.1209	–1.1719	–1.2222
0.7000	–0.6901	–0.7152	–0.7422	–0.7690	–0.7966	–0.8243	–0.8541
0.8000	–0.3001	–0.3161	–0.3329	–0.3503	–0.3679	–0.3844	–0.4030
0.8999	–0.0898	–0.0974	–0.1064	–0.1146	–0.1243	–0.1342	–0.1445
				[Ch][CPC] (1) + Ethanol (2)			
				ρ/g·cm^{-3}			
0.0000	0.789921	0.785631	0.781313	0.776961	0.772569	0.768129	0.763643
0.1000	0.883761	0.880058	0.876346	0.872620	0.868882	0.865346	0.861675
0.2000	0.941296	0.937876	0.934456	0.931034	0.927610	0.924175	0.920729
0.3000	0.980491	0.977241	0.973993	0.970744	0.967493	0.964241	0.961028
0.3999	1.009161	1.006035	1.002907	0.999781	0.996653	0.993519	0.990377
0.5001	1.031159	1.028152	1.025132	1.022098	1.019059	1.016017	1.012964
0.5992	1.048049	1.045022	1.041989	1.039004	1.036073	1.033125	1.030170
0.7000	1.062087	1.059122	1.05616	1.053198	1.050244	1.047289	1.044338
0.7986	1.073668	1.070713	1.067766	1.06483	1.0619	1.058956	1.056007
0.9001	1.083359	1.080470	1.077581	1.074698	1.071818	1.068938	1.066058
1.0000	1.092476	1.089616	1.086760	1.083909	1.081066	1.078224	1.075387
				V^E/cm^3·mol^{-1}			
0.1000	–0.8825	–0.9206	–0.9606	–1.0026	–1.0472	–1.1133	–1.1725
0.2000	–1.1229	–1.1711	–1.2218	–1.2754	–1.3322	–1.3922	–1.4552
0.3000	–1.1290	–1.1782	–1.2299	–1.2841	–1.3410	–1.4017	–1.4701
0.3999	–1.0457	–1.0930	–1.1420	–1.1935	–1.2472	–1.3034	–1.3618
0.5001	–0.9139	–0.9608	–1.0076	–1.0544	–1.1024	–1.1528	–1.2042
0.5992	–0.7120	–0.7416	–0.7715	–0.8092	–0.8555	–0.9017	–0.9487
0.7000	–0.5053	–0.5290	–0.5537	–0.5792	–0.6063	–0.6348	–0.6650
0.7986	–0.3255	–0.3367	–0.3493	–0.3638	–0.3790	–0.3930	–0.4065
0.9001	–0.0735	–0.0812	–0.0886	–0.0966	–0.1043	–0.1124	–0.1203

Table 3. Coefficients of the Redlich−Kister Equation for V^E of [Ch][CHC] (1) + Ethanol (2) and [Ch][CPC] (1) + Ethanol (2) Systems

systems	T/K	A_0	A_1	A_2	A_3	σ
[Ch][CHC] (1) + Ethanol (2)	293.15	–5.3618	5.7403	–1.0966	1.1391	0.0611
	298.15	–5.5377	5.9251	–1.2261	1.1921	0.0636
	303.15	–5.7174	6.1157	–1.3774	1.2434	0.0659
	308.15	–5.9069	6.3164	–1.5240	1.3092	0.0677
	313.15	–6.1163	6.5267	–1.6649	1.3746	0.0685
	318.15	–6.3406	6.7375	–1.8037	1.4754	0.0690
	323.15	–6.5731	6.9602	–1.9597	1.5788	0.0699
[Ch][CPC] (1) + Ethanol (2)	293.15	–3.5400	2.8907	–2.7300	4.1690	0.0191
	298.15	–3.6975	3.0447	–2.8613	4.2594	0.0206
	303.15	–3.8596	3.2032	–3.0041	4.3655	0.0222
	308.15	–4.0335	3.3553	–3.1516	4.4985	0.0232
	313.15	–4.2216	3.4946	–3.2958	4.6865	0.0235
	318.15	–4.3975	3.5811	–3.6107	5.1723	0.0276
	323.15	–4.5930	3.7332	–3.8510	5.4902	0.0298

where n was the number of experimental data and p was the number of coefficients of the Redlich−Kister equation. Generally, the V^E are correlated by the three-term Redlich−Kister equation, namely $k = 3$. To obtain better correlation results, the three-term and five-term Redlich−Kister equations were used at the same time to correlate the V^E in our work. The results suggested there was little difference of standard deviation of V^E between them. So the three-term Redlich−Kister equation was selected as the correlation function for V^E in this work.

The data of excess molar volume were also presented in Table 2. The excess molar volume versus the mole fraction of NAILs was plotted in Figures 1 and 2. The values of the parameters A_i and standard deviations σ were listed in Table 3.

The excess molar volumes were negative over the entire composition range for the two binary systems, and the absolute values of excess molar volumes increased slightly with increasing temperature from (293.15 to 323.15) K. A minimum value in excess molar volumes of two systems was located at 0.3 and 0.4, respectively. A similar phenomenon has been observed by Mohammed,[34] Gao,[35] and Marta.[36] The negative excess molar volumes indicated that a more efficient packing and/or attractive interaction occurred when NAILs and the ethanol were mixed.

Generally, the high negative deviations from ideality in these two binary systems were due to the interstitial accommodation and strong intermolecular interactions such as electrostatic, dipole, and hydrogen bonding of the NAILs with ethanol. On the other hand, Hoblrey et al.[37,38] found that ionic liquids exhibited liquid clathrate formation in solvents with various ratios, and ratio was corresponded to the minimum value. From the experimental data, we could deduce that clathrate formation was also probably formed in two systems, [Ch][CHC] and [Ch][CPC], with ethanol, respectively.

Conclusion

The densities of two binary systems for biodegradable naphthenic acid ionic liquids, [Ch][CHC] and [Ch][CPC], with ethanol were measured by the Anton Paar DMA 5000 vibrating-tube densimeter over the whole range of compositions from (293.15 to 323.15) K. The excess molar volumes of two systems were obtained from experimental data and fitted to the Redlich−Kister equation. Estimated coefficients and standard error values were also presented, and all excess molar volumes were negative. A minimum value in excess molar volumes of two systems was located at 0.3 and 0.4, respectively.

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