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Molar heat capacities for (2-methyl-2-butanol + heptane) mixtures and cyclopentanol at temperatures from (284 to 353) K

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ABSTRACT

Isobaric specific heat capacities were measured for (2-methyl-2-butanol + heptane) mixtures and cyclopentanol within the temperature range from (284 to 353) K, and for 2-methyl-2-butanol in the (284 to 368) K temperature interval by means of a differential scanning calorimeter. The excess molar heat capacities were calculated from the experimental results. For the temperature range from (284 to 287) K, the excess molar heat capacity is S-shaped with negative values in the 2-methyl-2-butanol rich region and with small negative values at low alcohol concentrations at temperatures from (295 to 353) K. The excess molar heat capacities are positive for all compositions under test at temperatures from (288 to 294) K. The results are explained in terms of the influence of the molecular size and configuration of the alkanols on their self-association capability and of the change in molecular structure of the (2-methyl-2-butanol + heptane) mixtures. The differences between the temperature dependences of the heat capacities of the mixtures studied are qualitatively consistent with results obtained by Rappon et al. [M. Rappon, J.M. Greer, J. Mol. Liq. 33 (1987) 227–244; M. Rappon, J.A. Kaukinen, J. Mol. Liq. 38 (1988) 107–133; M. Rappon, R.M. Johns, J. Mol. Liq. 40 (1989) 155–179; M. Rappon, R.T. Syvitski, K.M. Ghazalli, J. Mol. Liq. 62 (1994) 159–179; M. Rappon, R.M. Johns, J. Mol. Liq. 80 (1999) 65–76; M. Rappon, S. Gillson, J. Mol. Liq. 128 (2006) 108–114].

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1. Introduction

The capability of formation of hydrogen-bonds and the type of the associates formed depend on the molecular configuration. Therefore pentanols and their mixtures with non-polar solvents have been chosen for the study of the influence of the chain structure and the position of the hydroxyl group in the alcohol molecule on their thermodynamic properties. Mixtures of this type are of particular interest from the point of view of the self-association of alkanols, of non-specific physical interactions between real species present in the mixture and of interstitial accommodation of alkane molecules in the alkanol multimer structure. Those features lead to excesses in the following molar quantities: heat capacity, enthalpy, Gibbs free energy, volume, entropy, isentropic compressibility, and internal pressure. All these quantities are strongly dependent on temperature.

The heat capacity is a very sensitive indicator of the structure of pure liquids and solutions. Cerdeiriña *et al.* [7] pointed out that the association effects are exemplified by the different experimental temperature dependence of C_p for pure associated liquids. Cerdeiriña *et al.* [8] concluded also that C_p (T) is governed by the association energy of the molecules, their self-association capability and molecular size.

The heat capacity of (alcohol + alkane) mixtures is useful for the understanding of the self-association of alcohol molecules in solutions [7,9–16]. Mixtures of alkanols with alkanes are liquid systems most frequently studied under atmospheric pressure. However, excess molar properties are reported mainly for alkan-1-ols with alkanes. Relatively few results of the temperature dependence of excess properties of (branched alkanol + alkane) mixtures, especially of this dependence of excess molar heat capacities, are available in the literature. To the best of our knowledge, the temperature dependence of the excess molar heat capacity has been reported only for (3-methyl-3-pentanol + decane) mixtures. The C_p of the above system over the whole composition range at T = (283.15, 298.15, 313.15, and 323.15) K has been reported by Costas and Patterson [11]. The excess molar heat capacity of three mixtures of (3-methyl-3-pentanol + decane) for the temperature range from (278.15 to 338.15) K in 2.5 K steps has been also reported by Cerdeiriña *et al.* [15]. Moreover Cerdeiriña *et al.* [7,8,15] proposed a two-state association model which is able to describe temperature dependence of heat capacities for pure alcohols and (alcohol + alkane) mixtures. The excess molar heat

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TABLE 1
Comparison of the molar heat capacities, refractive indices, and densities of the pure components at $T = 298.15$ K under atmospheric pressure obtained in this work with those reported in the literature.

Component		This work	Literature
Heptane[a]	n_D	1.3852	1.3851 [18], 1.3852 [19,20], 1.3853 [21], 1.3855 [22]
	$\rho/(\mathrm{kg \cdot m^{-3}})$	679.53	679.48 [23], 679.56 [21], 679.57 [24], 679.60 [25], 679.7 [26]
2-Methyl-2-butanol	n_D	1.4025	1.40237 [27], 1.40238 [28,29], 1.4024 [30]
	$\rho/(\mathrm{kg \cdot m^{-3}})$	804.32	804.25 [31], 804.257 [32], 804.33 [33,34], 804.37 [35], 804.5 [28,30]
	$C_{p,m}/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	247.44	242.96 [36], 247.61 [17], 251.1 [37]
Cyclopentanol	n_D	1.4512	1.4505 [38], 1.45159 [38]
	$\rho/(\mathrm{kg \cdot m^{-3}})$	942.86	942.91 [38], 942.97 [35]
	$C_{p,m}/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	181.82	182.21 [17]

[a] Comparison of C_p was given in [16].

TABLE 2
Experimental molar heat capacities of $\{x_1$ 2-methyl-2-butanol + $(1 - x_1)$ heptane$\}$ within the temperature range (284 to 353) K at atmospheric pressure.

T/K	$C_{p,m}/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	T/K	$C_{p,m}/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	T/K	$C_{p,m}/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	T/K	$C_{p,m}/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$
	$x_1 = 0.0061$				$x_1 = 0.0249$		
284.14	220.41	319.15	232.58	284.14	226.02	319.16	235.12
285.15	220.65	320.14	232.92	285.15	226.27	320.14	235.28
286.16	220.90	321.15	233.36	286.16	226.64	321.15	235.64
287.14	221.16	322.15	233.83	287.14	226.92	322.15	235.95
288.15	221.55	323.14	234.21	288.15	227.34	323.14	236.15
289.14	221.82	324.15	234.52	289.14	227.63	324.15	236.43
290.14	222.02	325.15	234.92	290.14	227.88	325.15	236.80
291.15	222.40	326.14	235.39	291.15	228.24	326.14	237.10
292.14	222.70	327.15	235.69	292.16	228.51	327.15	237.39
293.14	223.05	328.15	236.22	293.14	228.85	328.15	237.72
294.15	223.39	329.14	236.63	294.15	229.18	329.14	238.11
295.14	223.70	330.14	237.14	295.14	229.37	330.15	238.44
296.14	223.96	331.15	237.49	296.14	229.63	331.15	238.70
297.15	224.33	332.14	237.91	297.15	229.81	332.14	239.06
298.14	224.65	333.14	238.38	298.14	230.08	333.14	239.45
298.16	224.66	334.15	238.94	298.16	230.09	334.04	239.87
299.14	224.99	335.14	239.28	299.14	230.35	334.33	239.98
300.15	225.26	336.14	239.67	300.15	230.51	335.14	240.20
301.14	225.70	337.15	240.08	301.16	230.74	336.14	240.60
302.14	226.13	338.14	240.60	302.14	231.02	337.15	241.00
303.15	226.42	339.14	241.00	303.15	231.23	338.14	241.26
304.14	226.83	340.15	241.53	304.16	231.50	339.14	241.65
305.14	227.18	341.16	241.89	305.14	231.73	340.15	242.15
306.15	227.53	342.14	242.38	306.15	231.92	341.14	242.51
307.14	227.97	343.15	242.71	307.16	232.13	342.14	242.91
308.14	228.36	344.16	243.26	308.14	232.33	343.15	243.18
309.15	228.70	345.14	243.73	309.15	232.53	344.16	243.63
310.16	229.11	346.15	244.11	310.16	232.84	345.14	244.12
311.14	229.41	347.16	244.48	311.14	233.01	346.15	244.51
312.15	229.87	348.14	244.95	312.15	233.27	347.16	244.81
313.16	230.16	349.15	245.31	313.16	233.44	348.14	245.23
314.14	230.54	350.15	245.70	314.14	233.76	349.15	245.69
315.15	231.04	351.14	246.16	315.15	234.10	350.16	245.90
316.16	231.41	352.15	246.53	316.16	234.24	351.14	246.29
317.14	231.74	353.15	246.79	317.14	234.45	352.15	246.70
318.15	232.22			318.15	234.79	353.15	247.03
	$x_1 = 0.0494$				$x_1 = 0.1000$		
284.14	229.40	319.15	240.63	284.16	232.58	319.15	249.49
285.15	229.86	320.14	240.72	285.15	233.16	320.14	249.68
286.16	230.34	321.15	240.94	286.16	233.84	321.15	249.94
287.14	230.72	322.15	241.13	287.14	234.39	322.15	250.19
288.15	231.29	323.14	241.26	288.15	235.13	323.14	250.37
289.14	231.74	324.15	241.45	289.14	235.73	324.15	250.60
290.14	232.10	325.15	241.60	290.14	236.25	325.15	250.76
291.15	232.63	326.14	241.80	291.15	236.91	326.14	250.96
292.14	233.02	327.15	241.94	292.14	237.52	327.15	251.07
293.14	233.49	328.15	242.15	293.14	238.13	328.15	251.24
294.15	233.86	329.14	242.34	294.15	238.71	329.14	251.42
295.14	234.25	330.15	242.58	295.14	239.22	330.14	251.61
296.14	234.59	331.15	242.66	296.14	239.76	331.15	251.73
297.15	235.01	332.14	242.88	297.15	240.36	332.14	251.74
298.14	235.35	333.14	243.08	298.14	240.89	333.14	251.95
298.16	235.36	334.15	243.42	298.16	240.91	334.15	252.08
299.14	235.67	335.14	243.54	299.14	241.48	335.14	252.23
300.15	236.00	336.14	243.78	300.15	241.90	336.14	252.29

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