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Excess molar volumes of nitrile + ketone mixtures at 298.15 K

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Abstract

Excess molar volumes of twelve binary nitrile + ketone mixtures (acetonitrile, butyronitrile or pentanenitrile + propanone, + butanone, + 2-pentanone or + 3-pentanone) have been determined from density measurements at 298.15 K using a vibrating-tube densitometer. Excess molar volumes for these mixtures are negative except for butyronitrile or pentanenitrile + propanone.

Keywords: Binary system; Density; Excess molar volume; Ketone; Nitrile

1. Introduction

Following our studies on the thermodynamics of binary mixtures containing organic nitrogen compounds [1–5], we report on the experimental excess molar volumes at 298.15 K for binary mixtures of a nitrile (acetonitrile, butyronitrile or pentanenitrile) and a ketone (propanone, butanone, 2-pentanone or 3-pentanone). As far as we know, the available experimental volumetric data on these mixtures are scarce and are limited to acetonitrile [6–9]. Our measurements of excess molar volumes of acetonitrile + propanone, at 298.15 K, agree very well with those reported by Brown and Smith [6] and Grolier et al. [7], but are noticeably more negative than those of Mato and Fernández-Polanco [8]. Dharmaraju et al. [9] have

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Table 1
Refractive index n_D and density ρ for the pure nitriles and ketones at 298.15 K

Component	n_D(exp)	n_D(ref.)	ρ(exp.)/ (kg m^{-3})	ρ(ref. 10)/ (kg m^{-3})
Acetonitrile	1.34255	1.3416	776.259	776.6
Butyronitrile	1.38217	1.3820	785.909	786.5
Pentanenitrile	1.39475	1.3951	794.433	795.0
Propanone	1.35769	1.35596	784.087	785.47
Butanone	1.37670	1.3764	800.543	800.02
2-Pentanone	1.38836	1.3880	801.715	802.54
3-Pentanone	1.39005	1.39002	809.003	809.45

reported excess molar volumes of acetonitrile + aliphatic and cycloaliphatic ketones at 303.15 K.

2. Experimental

2.1. Materials

The liquids used were butyronitrile and 2-pentanone (Fluka AG Buchs, better than 99 mol%), butanone and 3-pentanone (Fluka AG Buchs, better than 99.54 mol%), acetonitrile and propanone (Aldrich, better than 99.9 mol%), and pentanenitrile (Aldrich, better than 99.5 mol%). All the liquids were used directly without further purification. The densities and refractive indices of these samples are listed in Table 1 along with other literature values.

2.2. Excess molar volumes

Excess molar volumes V_m^E were calculated from density measurements, at 298.15 K, carried out in a vibrating-tube digital densitometer (Anton-Paar model DMA 60) equipped with a DMA 602 cell. The densitometer calibration was performed, at atmospheric pressure, by using doubly distilled and degassed water, benzene, and dried air. The vibrating-tube temperature was measured by means of an Anton-Paar DM 100-30 digital thermometer and was regulated to better than 0.01 K using a Neslab RTE-210 thermostat. Mixtures were prepared by mass, the mole-fraction error being estimated to be less than 10^{-4}. Duplicate densities of pure liquids and mixtures studied agreed to within $\pm 2 \times 10^{-5}$ g cm^{-3}.

3. Results and discussion

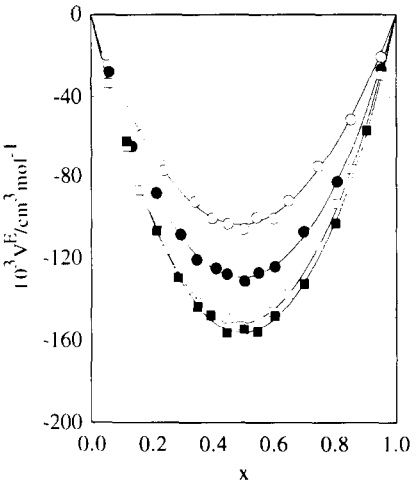
The calculated values of the excess molar volume V_m^E for the studied mixtures are listed in Table 2 and plotted against x in Figs. 1 and 2. Each set of results was fitted by the ordinary (unweighted) least-squares method to a polynomial

Table 2
Experimental density ρ and excess volume V_m^E for the studied mixtures at 298.15 K

x	ρ/ (kg m^{-3})	V_m^E/ (cm^3 mol^{-1})	x	ρ/ (kg m^{-3})	V_m^E/ (cm^3 mol^{-1})
Acetonitrile + propanone					
0.0576	784.060	−0.0279	0.5031	782.414	−0.1306
0.1322	784.025	−0.0641	0.5495	782.029	−0.1265
0.2124	783.809	−0.0875	0.6035	781.587	−0.1236
0.2927	783.545	−0.1077	0.6989	780.606	−0.1064
0.3451	783.359	−0.1203	0.8011	779.396	−0.0818
0.4085	782.993	−0.1245	0.9508	777.171	−0.0266
0.4449	782.780	−0.1273			
Acetonitrile + butanone					
0.0558	800.034	−0.0336	0.4887	793.499	−0.1526
0.1157	799.409	−0.0642	0.5509	792.065	−0.1483
0.1552	789.997	−0.0863	0.5969	790.945	−0.1455
0.2463	797.774	−0.1156	0.6472	789.589	−0.1370
0.3118	796.809	−0.1347	0.7467	786.585	−0.1135
0.3543	796.086	−0.1410	0.8080	784.466	−0.0926
0.4399	794.471	−0.1477	0.8541	782.750	−0.0758
0.4469	794.338	−0.1487	0.9522	778.595	−0.0297
Acetonitrile + 2-pentanone					
0.0491	801.232	−0.0194	0.5411	793.370	−0.0994
0.1607	799.998	−0.0586	0.5993	791.979	−0.0998
0.2379	798.971	−0.0764	0.6473	790.631	−0.0910
0.3383	797.418	−0.0916	0.7459	787.547	−0.0742
0.3955	796.440	−0.0998	0.8521	783.550	−0.0509
0.4475	795.440	−0.1024	0.9504	778.986	−0.0205
0.4999	794.361	−0.1050			
Acetonitrile + 3-pentanone					
0.1139	807.534	−0.0617	0.5029	799.601	−0.1540
0.2142	805.997	−0.1059	0.5460	798.366	−0.1555
0.2830	804.773	−0.1290	0.6047	796.451	−0.1474
0.3477	803.456	−0.1430	0.7000	792.944	−0.1321
0.3915	802.455	−0.1472	0.8013	788.432	−0.1023
0.4451	801.189	−0.1562	0.9035	782.814	−0.0564
Butyronitrile + propanone					
0.1000	784.239	0.0059	0.5004	784.888	0.0195
0.1984	784.377	0.0122	0.5670	785.047	0.0156
0.2893	784.519	0.0161	0.6022	785.110	0.0155
0.3429	784.620	0.0165	0.7106	785.321	0.0131
0.3955	784.693	0.0193	0.8008	785.522	0.0077
0.4479	784.806	0.0179	0.9143	785.751	0.0027
Butyronitrile + butanone					
0.1099	799.210	−0.0271	0.5157	793.670	−0.0657
0.1488	798.734	−0.0365	0.5543	793.109	−0.0662
0.2421	797.529	−0.0522	0.5975	792.452	−0.0637
0.2999	796.757	−0.0594	0.7021	790.797	−0.0510
0.3502	796.070	−0.0642	0.8122	789.062	−0.0392
0.3848	795.579	−0.0655	0.8747	788.004	−0.0250
0.4509	794.618	−0.0658	0.9122	787.393	−0.0192
0.5010	793.877	−0.0647			

Table 2 (continued)

x	ρ/ (kg m^{-3})	V_m^E/ (cm^3 mol^{-1})	x	ρ/ (kg m^{-3})	V_m^E/ (cm^3 mol^{-1})
Butyronitrile + 2-pentanone					
0.0523	801.154	−0.0162	0.5023	795.127	−0.0691
0.1041	800.567	−0.0296	0.5529	794.294	−0.0645
0.2119	799.267	−0.0521	0.6073	793.393	−0.0612
0.3154	797.881	−0.0628	0.7011	791.773	−0.0534
0.4022	796.636	−0.0668	0.8015	789.974	−0.0458
0.4511	795.920	−0.0696	0.9018	787.989	−0.0256
Butyronitrile + 3-pentanone					
0.1006	807.425	−0.0486	0.5471	798.325	−0.1032
0.1986	805.668	−0.0751	0.6031	796.999	−0.1015
0.3134	803.462	−0.0979	0.7030	794.493	−0.0904
0.3997	801.682	−0.1079	0.8020	791.800	−0.0668
0.4440	800.715	−0.1092	0.9075	788.783	−0.0383
0.5068	799.267	−0.1052			
Pentanenitrile + propanone					
0.0883	785.130	0.0198	0.5040	789.687	0.0565
0.0961	785.178	0.0255	0.5545	790.205	0.0550
0.2029	786.408	0.0425	0.6027	790.684	0.0535
0.3192	787.691	0.0552	0.7006	791.671	0.0434
0.3552	788.105	0.0550	0.8027	792.657	0.0303
0.3834	788.420	0.0550	0.8961	793.515	0.0171
0.4537	789.144	0.0589			
Pentanenitrile + butanone					
0.1102	799.888	−0.0130	0.5294	797.285	−0.0250
0.1895	799.437	−0.0231	0.5648	797.045	−0.0216
0.2870	798.840	−0.0287	0.6481	796.532	−0.0191
0.3416	798.423	−0.0212	0.7556	795.872	−0.0138
0.4069	798.019	−0.0223	0.8437	795.351	−0.0100
0.4416	797.815	−0.0239	0.9133	794.950	−0.0071
Pentanenitrile + 2-pentanone					
0.0497	801.399	−0.0050	0.5053	798.363	−0.0371
0.1005	801.090	−0.0120	0.5512	798.041	−0.0387
0.2032	800.410	−0.0192	0.6075	797.627	−0.0384
0.2979	799.769	−0.0244	0.7079	796.863	−0.0348
0.4020	799.119	−0.0380	0.8092	796.065	−0.0281
0.4511	798.768	−0.0386	0.9020	795.285	−0.0160
Pentanenitrile + 3-pentanone					
0.0423	808.516	−0.0157	0.5059	802.275	−0.0762
0.1433	807.233	−0.0379	0.5469	801.656	−0.0735
0.2460	805.942	−0.0627	0.6497	800.097	−0.0662
0.3480	804.559	−0.0749	0.7492	798.611	−0.0626
0.4092	803.694	−0.0779	0.8497	796.965	−0.0407
0.4486	803.129	−0.0788	0.9506	795.296	−0.0173



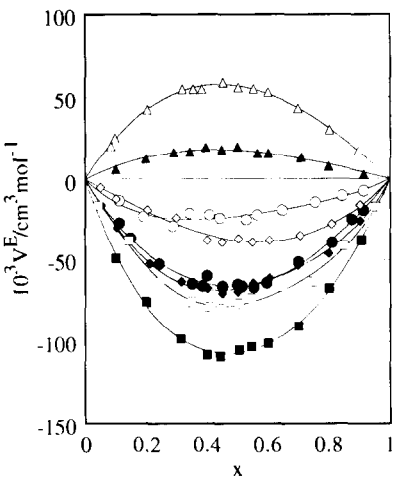


Fig. 1. Excess molar volume V_m^E at 298.15 K of acetonitrile + propanone (●); + butanone (□); + 2-pentanone (○); + 3-pentanone (■). Curves calculated from eqn. (1) with coefficients from Table 3.

Fig. 2. Excess molar volumes V_m^E at 298.15 K of butyronitrile + propanone (▲); + butanone (●); + 2-pentanone (◆); + 3-pentanone (■); and pentanenitrile + propanone (△); + butanone (○); + 2-pentanone (◇); + 3-pentanone (□). Curves calculated from eqn. (1) with coefficients from Table 3.

$$V_m^E/(cm^3\ mol^{-1}) = x(1-x)\sum A_i(2x-1)^i \quad (1)$$

the parameters of which, along with the standard deviations σ, given by

$$\sigma(V_m^E) = \left[\sum (V^E - V_{exp}^E)^2/(N-n)\right]^{1/2} \quad (2)$$

where N is the number of experimental points and n the number of coefficients A_i, are listed in Table 3.

The excess molar volumes V_m^E for the studied nitrile + ketone mixtures are negative at all compositions except for butyronitrile or pentanenitrile + propanone, and decrease (became more negative) as the number of carbon atoms in the ketone molecule increases, following the sequence: V_m^E of nitrile + propanone > nitrile + butanone > nitrile + 3-pentanone. This order shows that the increase in aliphatic chain length of the ketone ("dilution effect" of the carbonyl group in the molecule) decreases the interaction between unlike molecules. However, for a given ketone, V_m^E decreases with decreasing number of alkyl groups (and increasing dipole moment) in the nitrile molecule, falling in the sequence: V_m^E of ketone + pentanenitrile > ketone + butyronitrile > ketone + acetonitrile.

The volumetric behaviour shown by these systems indicates that dipole interactions might not be the only cause of the deviations. Comparing the V_m^E values of the nitrile + ketone mixtures studied with the corresponding nitrile + alkane or ketone + alkane mixtures [11, 12], a noticeable contraction is observed, indicating an important contribution of the specific CN–CO interaction. In the case of

Table 3
Values of the coefficients A_i, Eq. (1), and standard deviations $\sigma(V_m^E)$, Eq. (2), of experimental molar excess volumes V_m^E for nitrile(1) + ketone(2) mixtures at 298.15 K

Mixture	A_1	A_2	A_3	A_4	$\sigma(V_m^E)/(cm^3\ mol^{-1})$
Acetonitrile +					
propanone	−0.5155	0.0149	−0.0238		0.0017
butanone	−0.6036	0.0253	−0.0415		0.0015
2-pentanone	−0.4109	0.0209			0.0017
3-pentanone	−0.6233	0.0152	−0.0245	−0.0631	0.0016
Butyronitrile +					
propanone	0.0696	−0.0212			0.0013
butanone	−0.2662	0.0343			0.0013
2-pentanone	−0.2692	0.0564	−0.0639	−0.0699	0.0015
3-pentanone	−0.4285	0.0485	−0.0825		0.0020
Pentanenitrile +					
propanone	0.2285	−0.0538			0.0013
butanone	−0.0923	0.0470	−0.0424		0.0025
2-pentanone	−0.1524	−0.0455			0.0019
3-pentanone	−0.3085	0.0531	−0.0508	−0.1109	0.0026

acetonitrile + propanone, the presence of hydrogen bonding between the oxygen of ketone and the hydrogen of acetonitrile [6] has been proposed.

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