and Figure 1), concerning the behavior of V_2° and $\bar{v}_2$ as a function of the number of CH_2 groups in nitrile molecules, would prompt us to enter into a discussion on the suitability of one or another theory, based on group-contribution models, in interpretating experimental data. Moreover, our measurements were carried out at 303.16 K, as reported above, whereas most of the literature data on the subject refer to measurements, on aqueous solutions, at 298.16 K. Therefore, we think that, for a more detailed discussion and a more complete and self-consistent review of literature data, for the sake of comparison, measurements on dilute aqueous nitrile solutions are needed, at 298.16 K, which will be the subject of the next paper.

Acknowledgment

We are indebted to Luigi Lisbo Parrella for technical assistance.

Registry No. Sulfolane, 126-33-0; acetonitrile, 75-05-8; propionitrile, 107-12-0; butyronitrile, 109-74-0; valeronitrile, 110-59-8; 2-methylpropionitrile, 78-82-0; 2,2-dimethylpropionitrile, 630-18-2.

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Partial Molar Volumes of C_2–C_6 *n*-Alkanenitriles and Octanenitrile in Dilute Aqueous Solutions at 298.16 K

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Partial molar volumes, $\bar{v}_2$, of acetonitrile, propionitrile, butyronitrile, valeronitrile, and hexane- and octanenitriles were measured in dilute aqueous solutions, at 298.16 K. Experimental data were correlated to van der Waals volumes, v_w, calculated from thermal data. Equations of the kind $V = av_w + b$ ($a \simeq 1.55$) were found to be suitable in reproducing both volumes of pure substances and partial molar volumes of solutes in dilute solutions within the limits of experimental errors. The above correlation may be interpreted in terms of an impenetrable volume larger than v_w, presumably because of intrinsic geometrical factors, which result in reducing the empty volume involved in interactions. Data on nitriles are analyzed in the light of current theories based on group-contribution models.

Introduction

In a previous note (*1*) we presented data on partial molar volumes, $\bar{v}_2$, of normal and branched C_2–C_5 alkanenitriles in dilute sulfolane solutions, at 303.16 K. Some regularities were observed concerning the CH_2 and CH_3 group contributions both to volume V_2° of pure nitriles and to $\bar{v}_2$ of nitriles as solutes, as expected.

Furthermore, on the basis of the supposition that only the empty volume of a molecule, v_e ($\simeq V^\circ - v_w$, to first approximation), could be modified by interactions of any kind, we calculated the van der Waals volumes, v_w, from thermal data by means of an improved method proposed by one of us (*2*).

We suggested as well a possible criterion for evaluating the relative extent of solute–solvent interactions and solute–solute interactions and hence for classifying the solvent as structure making or breaking. We preferred however, at that time, not to enter into a discussion on the suitability of one or another of current theories (*3–5*) based on group-contribution models. We proposed the interpretation of experimental data, after the completion of the picture of nitrile series behavior by means of analogous measurements on aqueous solutions. This is the subject of the present note.

Experimental Section

Conductivity water was obtained by repeated distillations over $KMnO_4$ after passage through a mixed-bed ion-exchange-resin column. The conductance of samples collected and stored after degassing, in all-Pyrex glassware, routinely ranged between 0.4×10^{-6} and 1×10^{-6} Ω^{-1} cm^{-1}.

C_2–C_5 n-Alkanenitriles (J. T. Baker Chemical Co.) were purified as reported previously (*6*). Hexane- and octanenitriles (Aldrich Chemical Co.) were purified by repeated distillation over P_2O_5.

The properties (density, dielectric constants, melting points) of the samples agreed with the most reliable literature data (*7*).

Solutions were made by weight (reduced to mass) and stored in dark containers. In the case of octanenitrile, because of its

Table I. Densities ($d_{1,2}$) and Volume ($V_{1,2}$)[a] of Water (1)-Acetonitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 298.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.000 00	0.997 043	1002.966		
0.002 39	0.997 01	1003.097	54.812	49.372
0.017 30	0.996 92	1003.802	48.324	47.572
0.049 30	0.996 72	1005.321	47.769	47.505
0.113 00	0.996 33	1008.340	47.558	47.442
0.176 63	0.995 94	1011.357	47.506	47.432
0.249 86	0.995 50	1014.824	47.459	47.407
0.303 94	0.995 17	1017.392	47.463	47.421
0.373 78	0.994 75	1020.703	47.453	47.418
0.428 62	0.994 42	1023.306	47.455	47.424
0.498 92	0.994 01	1026.632	47.434	47.408

[a] $V_{1,2} = 1002.979 + 47.416m$. [b] Solvent = water; solute = acetonitrile.

Table II. Densities ($d_{1,2}$) and Volumes ($V_{1,2}$)[a] of Water (1)-Propionitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 298.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.000 00	0.997 043	1002.966		
0.001 36	0.997 03	1003.054	64.706	64.706
0.007 61	0.996 97	1003.460	64.915	64.915
0.014 31	0.996 91	1003.890	64.570	64.570
0.045 49	0.996 63	1005.895	64.388	64.388
0.089 92	0.996 23	1008.756	64.391	64.391
0.137 17	0.995 82	1011.785	64.292	64.292
0.188 81	0.995 35	1015.120	64.372	64.372
0.225 60	0.995 06	1017.452	64.211	64.211
0.278 51	0.994 56	1020.894	64.371	64.371
0.330 66	0.994 10	1024.223	64.403	64.403
0.376 21	0.993 70	1027.193	64.398	64.398

[a] $V_{1,2} = 1002.966 + 64.336m$. [b] Solvent = water; solute = propionitrile.

Table III. Densities ($d_{1,2}$) and Volumes ($V_{1,2}$)[a] of Water (1)-Butyronitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 298.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.000 00	0.997 043	1002.966		
0.002 80	0.997 03	1003.173	73.929	78.214
0.008 49	0.996 97	1003.628	77.974	79.388
0.022 94	0.996 81	1004.791	79.555	80.078
0.034 64	0.996 65	1005.763	80.745	81.091
0.054 72	0.996 45	1007.358	80.263	80.482
0.066 88	0.996 29	1008.363	80.697	80.876
0.077 03	0.996 21	1009.148	80.254	80.410
0.097 30	0.995 97	1010.798	80.493	80.617
0.118 02	0.995 76	1012.449	80.351	80.452
0.178 16	0.995 08	1017.317	80.551	80.619

[a] $V_{1,2} = 1002.954 + 80.586m$. [b] Solvent = water; solute = butyronitrile.

Table IV. Densities ($d_{1,2}$) and Volumes ($V_{1,2}$)[a] of Water (1)-Valeronitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 298.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.000 00	0.997 043	1002.966		
0.004 80	0.996 98	1003.429	96.458	96.667
0.008 30	0.996 94	1003.762	95.904	96.024
0.009 50	0.996 92	1003.882	96.421	96.526
0.013 70	0.996 86	1004.292	96.788	96.861
0.016 60	0.996 82	1004.575	96.928	96.988
0.020 10	0.996 78	1004.907	96.567	96.617
0.021 80	0.996 75	1005.079	96.927	96.972
0.026 10	0.996 69	1005.498	97.011	97.050
0.028 60	0.996 67	1005.727	96.538	96.573
0.041 40	0.996 50	1006.966	96.618	96.643

[a] $V_{1,2} = 1002.965 + 96.728m$. [b] Solvent = water; solute = valeronitrile.

Table V. Densities ($d_{1,2}$) and Volumes ($V_{1,2}$)[a] of Water (1)-Hexanenitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 298.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.0000	0.997 043	1002.966		
0.0030	0.997 00	1003.301	111.667	111.667
0.0053	0.996 96	1003.566	113.208	113.208
0.0059	0.996 96	1003.624	111.525	111.525
0.0084	0.996 92	1003.908	112.143	112.143
0.0119	0.996 88	1004.290	111.261	111.261
0.0124	0.996 87	1004.348	111.452	111.452
0.0128	0.996 86	1004.397	111.797	111.797
0.0138	0.996 84	1004.515	112.246	112.246
0.0149	0.996 82	1004.642	112.483	112.483
0.0163	0.996 81	1004.789	111.840	111.840

[a] $V_{1,2} = 1002.966 + 111.911m$. [b] Solvent = water; solute = hexanenitrile.

Table VI. Densities ($d_{1,2}$) and Volumes ($V_{1,2}$)[a] of Water (1)-Octanenitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 298.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.0000	0.997 043	1002.966		
0.0006	0.997 03	1003.054	146.667	148.333
0.0013	0.997 02	1003.152	143.077	143.846
0.0016	0.997 01	1003.200	146.250	146.875
0.0021	0.997 00	1003.273	146.190	146.667
0.0026	0.996 99	1003.346	146.154	146.538

[a] $V_{1,2} = 1002.965 + 146.181m$. [b] Solvent = water; solute = octanenitrile.

very low solubility, particular care was taken in preparing solutions. Weighed nitrile samples were shaken vigorously with a massive weighed sample of solvent every 3 h for 2 or 3 days until homogeneous solutions were obtained.

The density-measuring apparatus and the temperature-controlling equipment were described elsewhere (*8*). The accuracy for density usually was better than 1×10^{-5} g cm^{-3}, but it was lower in the case of octane- and hexanenitrile solutions, whose reported values are the average of two or three measurements on each sample.

For each binary system 7–10 measurements were carried out at different molalities. The selected molalities were dictated by solubility in the case of the less soluble nitriles; in the other cases they ranged between 0.002 and 0.5 *m*. All measurements were carried out at 298.16 ∓ 0.001 K.

Results

The experimental values of density, $d_{1,2}^{298.16\mathrm{K}}$, and molalities, m, of the selected C_2–C_6 *n*-alkanenitriles and octanenitrile aqueous solutions are summarized in Tables I–VI, where also the average of densities $d_1^{298.16\mathrm{K}}$ of the solvent before and after each run is reported; from molalities and densities, the volumes $V_{1,2}$ of solutions were calculated and, for each temperature, the apparent molar volume of solute, ϕ_2, was derived by using the equation

$$\phi_2 = (V_{1,2} - 1000/d_1)/m \qquad (1)$$

In the selected molality range, ϕ_2 values do not depend on dilution; therefore, the partial molar volume $\bar{v}_2$ of the solute was calculated by smoothing equations of the type

$$V_{1,2} = 55.55\bar{v}_1 + \bar{v}_2 m \qquad (2)$$

$\bar{v}_1$ being the partial molar volume of water obtained by linear extrapolation of eq 2 at $m = 0$.

Table VII. Volumes, $V_2°$, of Pure Nitriles, Partial Volumes, $\bar{v}_2$ and $(\bar{v}_2)_S$ in Water and in Sulfolane, Respectively, $(\bar{v}_2)_S - \bar{v}_2$ Terms, and van der Waals Volumes, v_w, at T = 298.16 K

substance	$V_2°$	$\bar{v}_2$	$(\bar{v}_2)_S$	$(\bar{v}_2)_S - \bar{v}_2$	v_w
CH_3CN	52.863	47.416	51.57	4.15	27.75[a]
CH_3CH_2CN	70.925	64.336	69.24	4.87	38.15[a]
$CH_3(CH_2)_2CN$	87.898	80.586	85.49	4.90	48.08[a]
$CH_3(CH_2)_3CN$	107.600	96.728	101.58	4.85	59.24[a]
$CH_3(CH_2)_4CN$	121.285	111.911			69.64[b]
$CH_3(CH_2)_6CN$	154.701	146.181			90.84[b]

[a] From thermal data (*1*). [b] By extrapolation of values referring to lower numbers.

Table VIII. Parameters A_v and B_v of Linear Equations 3, 4, and 6 Correlating Volumes ($V°$, $\bar{v}$, and v_w) to the Number of CH_2 Groups in the Molecule at 298.16 K

homologous series	$A_{V°}$	$B_{V°}$	$A_{\bar{v}_2}$	$B_{\bar{v}_2}$	A_{v_w}	B_{v_w}	substance studied
alkanes	15.98	67.91 (*7, 13*)	14.55	57.38 (*4*)	10.45[a]	27.03[a]	C_5–C_{10}
alcohols	16.69	58.58 (*7*)	15.74	55.03 (*12*)	10.06[a]	30.37[a]	C_2–C_5
diols	16.32	55.81 (*7*)	16.04	55.63 (*4*)	10.33[a]	32.47[a]	C_2–C_5
ethers	16.78	54.20 (*7*)	16.10	48.28 (*4*)	10.24[a]	27.88[a]	$(C_2$–$C_5)_2$
amines	16.59	49.82 (*7, 9*)	15.88	42.26 (*9*)	10.23[b]	24.21[b]	C_3–C_7
nitriles	16.91	53.63 (this work)	16.34	47.61	10.53[a]	27.53[a]	C_2–C_8

[a] Thermal data. [b] Bondi's data.

Table IX. Homologous Series of Selected Substances for Testing of Theories for *a* and *b* Parameters of Linear Equations 3′ and 4′

homologous series		a	b	ref	a(aq)	b(aq)	members included in eq 3′ and 4′	ref
alkanes		1.52_9	26.49_6	*7, 13*	1.39_2	19.74_5	C_5–C_{10}	*4*
alcohols		1.65_9	8.20_6	*7*	1.56_4	7.52_3	C_2–C_5	*12*
diols		1.58_0	4.51_2	*14*	1.55_3	5.21_2	C_2–C_5	*4*
ethers		1.63_9	8.51_4	*7*	1.57_2	4.44_5	$(C_2$–$C_5)_2$	*4*
ammines		1.62_2	10.55_9	*7, 9*	1.55_2	4.67_9	C_4–C_7	*9*
nitriles	water	1.60_6	9.42_9	this work	1.55_2	4.88_6	C_2–C_8	this work
	sulfolane			*1*	1.57 (s)	8.55 (s)	C_2–C_5	*1*

Each table (Tables I–VI) reports the corresponding equation (eq 2) which reproduces experimental values of volume and hence of density within the limits of experimental error; also $\bar{v}_2$ values calculated by smoothing eq 2 are reported in each table. Both volumes, $V_2°$, and partial molar volumes, $\bar{v}_2$, in aqueous solutions exhibit a linear dependence on the number of CH_2 groups in the nitrile molecules. This behavior is reproduced by the equations

$$V_2° = 58.627 + 16.906n(CH_2) \qquad (3)$$

$$\bar{v}_2 = 47.612 + 16.343n(CH_2) \qquad (4)$$

In the case of pure nitriles, hence, a constant group contribution of 16.91 may be assigned to CH_2, in good agreement with literature data on homologous normal series which are scattered over 16.3 and 16.8 as reported by Cabani et al. (*9*). The corresponding datum in the case of dilute aqueous solutions is 16.34 and in dilute sulfolane solutions is 16.63. (Reasonably in the case of sulfolane solutions, the CH_2 group contribution has been calculated, at 298.16 K, from $\bar{v}_2$ values, measured at 303.16 K, on the supposition that the same temperature coefficient could be applied to both $V_2°$ and $\bar{v}_2$ data.)

For the sake of comparison data on nitriles in both sulfolane ($(\bar{v}_2)_S$) and aqueous ($\bar{v}_2$) solutions are summarized in Table VII together with the difference $(\bar{v}_2)_S - \bar{v}_2$; a constant shrinkage of 4.87 seems to accompany the transferring of 1 mol of nitrile from sulfolane to a dilute aqueous solution and this according to electrostatic and cage effects of water on polar solutes evidenced by previous literature (*10*).

Discussion

In our previous paper on this subject, we illustrated a method for calculating values of v_w starting from vaporization enthalpies; these values, which otherwise do not differ noticeably from Bondi's (*11*) data, reflect more faithfully, in our opinion, the real energetic situation of the molecule, since they are drawn from thermal data only. The calculated values of v_w for the first four members of the *n*-alkanenitrile series are reported in Table VII. In the case of hexane- and octanenitriles, for which thermal data are lacking, v_w values are calculated on ascribing to the CH_2 group a constant contribution of 10.53 as derived from data concerning lower nitriles.

As already pointed out, all the quantities $V_2°$, $\bar{v}_2$, $(\bar{v}_2)_S$, and v_w in Table VII exhibit indeed a linear dependence on $n(CH_2)$, i.e.

$$V_2° = 53.629 + 16.906n(CH_2) \qquad (3)$$

$$\bar{v}_2 = 47.612 + 16.343n(CH_2) \qquad (4)$$

$$(\bar{v}_2)_S = 52.07 + 16.629n(CH_2) \qquad (5)$$

$$v_w = 27.53 + 10.53n(CH_2) \qquad (6)$$

and more generally

$$V = B + An(CH_2) \qquad (7)$$

Then from equation pairs 3,6, 4,6, and 5,6, by easy mathematical arrangements, eq 3′–5′ are derived, which correlate respectively $V_2°$, $\bar{v}_2$, and $(\bar{v}_2)_S$ to van der Waals volumes, v_w. These equations are

$$V_2° = 1.606v_w + 9.429 \qquad (3')$$

$$\bar{v}_2 = 1.552v_w + 4.886 \qquad (4')$$

$$(\bar{v}_2)_{S'} = 1.579v_w + 8.552 \qquad (5')$$

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and more generally

$$V = av_w + b \qquad (7')$$

where the term $a = A/A_w = (V/v_w)_{CH_2}$ approximately is 1.6.

In eq 7′ the volume v_w appears indeed multiplied by a factor larger than unity, as if the impenetrable volume were larger than van der Waals volume, presumably because of intrinsic geometrical factors.

Therefore, the term $b = V - av_w$ may be identified with the volume really involved in interactions for all compounds containing a given functional group and it is constant along a series.

Reasonably all these conclusions are meaningful only in the limits of validity of the linear dependence on the number of CH_2 groups in the molecule of quantities which appear in eq 3-6.

Empirical equations like eq 7′ were found by previous authors (*3*, *4*) to be useful in reproducing experimental data in the case of series of homologous substances: cyclic and acyclic alcohols, ethers, ketones, diols, amines, etc.

In Tables VIII and IX the parameters of linear correlation A, B, a, and b are reported. For the sake of homogeneity the analysis is limited to the first four or five members of each homologous series, which are liquid in the standard state. As expected, the term a may be regarded as a constant, for both pure substances and dilute aqueous solutions. It reflects the constant contributions of CH_2 groups to V°, $\bar{v}_2$, and v_w. The term b on the contrary, is characteristic of each series, involving the effects of the functional group present in the molecule responsible for interactions. Therefore, the magnitude of the term b, as well as its change from a solvent to another, might be indicated as a criterion for detecting the extent of interactions of any kind and evidencing the structure-making or -breaking solvent effect.

As a general rule a shrinkage is indeed evidenced in transferring 1 mol of substance from pure state to a dilute aqueous solution according to the above-quoted water effects on polar solutes. Diols seem to be an exception since the term b is larger for water solutions (5.212) than for pure substances (4.512). This behavior is only apparently anomalous. The increase of the term b in aqueous solutions may well be ascribed to the destruction by water of hydrogen bonds between OH groups present in diol molecules, which counterbalance in excess the effects of interactions of diols with water.

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We are indebted to Luigi Lisbo Parrella for technical assistance.

Registry No. CH_3CN, 75-05-8; CH_3CH_2CN, 107-12-0; $CH_3(CH_2)_2CN$, 109-74-0; $CH_3(CH_2)_3CN$, 110-59-8; $CH_3(CH_2)_4CN$, 628-73-9; $CH_3(CH_2)_6CN$, 124-12-9.

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Binary Vapor–Liquid Equilibria of Carbon Dioxide with 2-Methyl-1-pentene, 1-Hexene, 1-Heptene, and *m*-Xylene at 303.15, 323.15, and 343.15 K

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Binary vapor–liquid equilibrium data at 303.15, 323.15, and 343.15 K for the systems CO_2–2-methyl-1-pentene, CO_2–1-hexene, CO_2–1-heptene, and CO_2–*m*-xylene measured in a static equilibrium cell are presented. The data were correlated by using the Peng–Robinson equation of state. The Peng–Robinson equation represents tha data well at all temperatures.

Introduction

Increased interest in tertiary oil recovery by carbon dioxide flooding, and extraction of coal as well as natural products by carbon dioxide, has encouraged studies of vapor–liquid equilibrium of carbon dioxide and unsaturated/aromatic hydrocarbon systems. Carbon dioxide–unsaturated hydrocarbon systems were previously neglected since they are not of primary importance to the petroleum industry, for which early carbon dioxide–hydrocarbon data were collected.

In this work, vapor–liquid equilibrium data are reported for the binary systems CO_2–2-methyl-1-pentene, CO_2–1-hexene, CO_2–1-heptene, and CO_2–*m*-xylene at 303.15, 323.15, and 343.15 K over a pressure range of 0–7.5 MPa. The data are reduced with the Peng–Robinson (*1*) equation of state. Temperature-independent parameters that allow interpolation of data are obtained.

Experimental Section

A schematic diagram of the apparatus is shown in Figure 1. The central unit was a blind, stainless-steel, constant-volume cell with an internal capacity of about 250 cm^3. The degassed

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