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VOLUMETRIC PROPERTIES OF BINARY MIXTURES OF ACRYLONITRILE WITH DIMETHYLSULFOXIDE (OR DIETHYLSULFOXIDE) AT TEMPERATURES FROM 298.15 TO 323.15K

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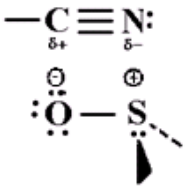
Densities, ρ, of binary solutions of acrylonitrile in polar aprotic solvents such as dimethylsulfoxide and diethylsulfoxide have been measured over the full range of compositions at temperatures from 298.15K to 323.15K. The excess molar volumes, $V_m{}^E$, apparent molar volumes, $V_{\phi,1}$, partial molar volumes, $\overline{V}_i$, excess partial molar volumes, $\overline{V}_i^E$ partial molar volumes at infinite dilution, V_i^∞, and thermal expansion coefficients, α_p, for binary liquid mixtures were calculated. The excess molar volumes are negative over the whole range of composition for these mixtures and become more negative with increasing temperatures from (298.15 to 323.15) K. The excess molar volumes were correlated by the Redlich–Kister equation. The obtained results were interpreted on the basis of dipole-dipole interactions between nitrile group of acrylonitrile and S=O group of dimethylsulfoxide or diethylsulfoxide.

Figs. 4, tables 6, references 19.

Acrylonitrile (AN) as a polar solvent serves as a monomer to synthesize polyacrylonitrile (PAN). It should be noted that interaction of solvent molecules with both PAN and AN takes place due to dipole-dipole interaction between nitrile group and polar groups of solvents [1-4]. Particularly, it was shown that penetration of solvent molecules into the polymer molecules occurs by breaking up the polar-polar interactions of the nitrile groups of PAN [1].

Moreover, interaction between $C \equiv N$ and $S = O$ groups leads to the negative values of excess molar volumes as it was shown in [5, 6] for dimethylsulfoxide (DMSO) - acetonitrile (ACN) binary mixtures. In addition, earlier on the basis of FT IR and Raman spectroscopic measurements of DMSO-ACN mixtures [7, 8] it was shown that the formation of the intermolecular associate as the antiparallel dipolar conformation takes place (Scheme 1).

Scheme 1.



It should be noted that although thermodynamic studies of binary mixtures of AN with some alkyl acetates, aromatic ketones, aromatic hydrocarbons and alkyl alcohols have been done by several authors [9-15] but to our knowledge there are no literature data for density and volumetric properties of AN-DMSO (or diethylsulfoxide (DESO)) binary systems.

This work reports densities and volumetric properties of binary mixtures of AN with DMSO, DESO and ACN from 298.15 to 323.15K over the entire composition range. A Redlich-Kister type equation correlates excess molar volumes. The excess molar volumes, V_m^E, apparent molar volumes, $V_{\phi,1}$, partial molar volumes, $\overline{V}_i$, excess partial molar volumes, $\overline{V}_i^E$ partial molar volumes at infinite dilution, V_i^∞, and thermal expansion coefficients, α_p, have been calculated as a function of composition.

Materials and Methods

AN was purchased from Aldrich Chemical Co. with >99% purity and content of 35-45ppm monomethyl ether hydroquinone as inhibitor.

DMSO (99.9% purity) and acetonitrile (>99% purity) were purchased from Aldrich Chemical Co. and were used without further purification.

DESO was prepared and purified according to procedure in ref. [16]. Its purity tested by gas chromatography (Carrier gas – *He*, Apiezon-Carbowax 20M, l=1*m*) was greater than 99.5 mass%; the water content, after drying on molecular sieves, was lower than 0.01 mass%.

The densities of solutions were measured on an Anton Paar DMA 4500 vibrating-tube densimeter in the temperature range of (298.15–323.15)K. The accuracy of the density and temperature measurements was $\pm 1\times10^{-2}$ *kg* m^{-3} and ±0.01K, respectively. The densimeter was calibrated with dry air and double-distilled water.

All solutions were prepared gravimetrically using a Sartorius CPA6235 balance with uncertainty of $\pm 1\times10^{-6}$*kg*.

Results and Discussion

From the experimental values of the densities volumetric properties: excess molar volume, V_m^E, apparent molar volume, $V_{\phi,1}$, partial molar volume, $\overline{V}_i$, excess

partial molar volume, $\overline{V}_i^E$ partial molar volume at infinite dilution, V_i^∞, and thermal expansion coefficient, α_p, were estimated.

Densities and Excess Molar Volumes.

The experimental values of densities of binary solutions of AN in DMSO, DESO and ACN at temperatures from 298.15 to 323.15K are listed in Table 1.

Table 1

Densities of binary solutions of AN(1) in DMSO, DESO and ACN (2) at T = (298.15-323.15) K

X_2	$\rho \times 10^{-3}\left(kg\ m^{-3}\right)$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
X(DMSO)			AN-DMSO			
0.0000	0.80079	0.79516	0.78949	0.78379	0.77806	0.77228
0.1056	0.83612	0.83061	0.82507	0.81950	0.81390	0.80826
0.2079	0.86860	0.86328	0.85784	0.85237	0.84688	0.84136
0.2988	0.89740	0.89207	0.88672	0.88135	0.87597	0.87059
0.3968	0.92719	0.92201	0.91669	0.91128	0.90591	0.90062
0.5016	0.95852	0.95334	0.94815	0.94295	0.93774	0.93250
0.5999	0.98702	0.98190	0.97678	0.97164	0.96649	0.96133
0.6986	1.01492	1.00997	1.00499	1.00005	0.99505	0.98980
0.7976	1.04235	1.03752	1.03267	1.02754	1.02255	1.01735
0.8979	1.06932	1.06431	1.05930	1.05429	1.04927	1.04425
1.0000	1.09562	1.09056	1.08556	1.08061	1.07560	1.07059
X(DESO)			AN-DESO			
0.0000	0.80079	0.79516	0.78949	0.78379	0.77806	0.77228
0.1014	0.83580	0.83038	0.82494	0.81947	0.81397	0.80844
0.1992	0.86561	0.86045	0.85520	0.84994	0.84464	0.83932
0.3033	0.89322	0.88823	0.88316	0.87807	0.87296	0.86782
0.4002	0.91684	0.91190	0.90697	0.90204	0.89708	0.89210
0.4927	0.93672	0.93199	0.92719	0.92238	0.91755	0.91270
0.6003	0.95705	0.95236	0.94767	0.94296	0.93824	0.93351
0.6914	0.97148	0.96686	0.96226	0.95765	0.95302	0.94839
0.7963	0.98721	0.98268	0.97817	0.97365	0.96912	0.96458
0.9003	1.00166	0.99730	0.99287	0.98844	0.98399	0.97953
1.0000	1.01398	1.00964	1.00528	1.00092	0.99654	0.99216
X(ACN)			AN-ACN			
0.0000	0.80079	0.79516	0.78949	0.78379	0.77806	0.77228
0.1011	0.79887	0.79326	0.78761	0.78193	0.77620	0.77044
0.2065	0.79694	0.79134	0.78571	0.78004	0.77434	0.76860
0.3060	0.79479	0.78921	0.78360	0.77795	0.77226	0.76654
0.4002	0.79273	0.78716	0.78157	0.77593	0.77026	0.76455
0.5002	0.79041	0.78486	0.77928	0.77367	0.76802	0.76234
0.6010	0.78798	0.78245	0.77690	0.77131	0.76568	0.76001
0.7015	0.78543	0.77993	0.77439	0.76882	0.76322	0.75758
0.7980	0.78289	0.77713	0.77163	0.76612	0.76061	0.75486
0.8969	0.78006	0.77430	0.76905	0.76354	0.75803	0.75228
1.0000	0.77662	0.77118	0.76572	0.76023	0.75471	0.74915

Excess molar volumes, V^E, of the above mentioned mixtures were calculated from the experimentally measured densities at each temperature using the following equation

$$V_m^E = (x_1 M_1 + x_2 M_2)/\rho - (x_1 M_1/\rho_1 + x_2 M_2/\rho_2) \quad (1)$$

where M_1 and M_2 represent the molar masses of AN and solvent (DMSO, DESO and ACN), respectively. The x_1 and x_2 are molar fractions of AN and solvent having densities ρ_1 and ρ_2 respectively.

As it follows from these data (Table 2) the excess molar volumes are negative over the whole range of composition and temperature for AN+DMSO (or DESO) binary mixtures and become more negative with increasing temperature from 298.15 to 323.15K, implying that the intermolecular forces between different molecules in those systems becomes more stronger (Fig. 1).

Table 2

Excess molar volumes, $V_m^E \times 10^6 \left(m^3 \cdot mol^{-1}\right)$, of binary solutions of AN (1) in (DMSO, DESO and ACN) (2) at T = (298.15-323.15) K

X_2	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
X(DMSO)			AN-DMSO			
0.0000	0.000	0.000	0.000	0.000	0.000	0.000
0.1056	-0.167	-0.180	-0.193	-0.206	-0.219	-0.234
0.2079	-0.222	-0.249	-0.270	-0.289	-0.311	-0.335
0.2988	-0.295	-0.320	-0.345	-0.370	-0.398	-0.431
0.3968	-0.308	-0.341	-0.364	-0.382	-0.406	-0.441
0.5016	-0.318	-0.346	-0.373	-0.400	-0.431	-0.463
0.5999	-0.295	-0.321	-0.348	-0.372	-0.400	-0.430
0.6986	-0.252	-0.284	-0.313	-0.343	-0.374	-0.389
0.7976	-0.201	-0.234	-0.263	-0.272	-0.294	-0.304
0.8979	-0.124	-0.136	-0.146	-0.153	-0.163	-0.174
1.0000	0.000	0.000	0.000	0.000	0.000	0.000
X(DESO)			AN-DESO			
0.0000	0.000	0.000	0.000	0.000	0.000	0.000
0.1014	-0.227	-0.238	-0.251	-0.263	-0.277	-0.292
0.1992	-0.395	-0.420	-0.440	-0.462	-0.485	-0.510
0.3033	-0.481	-0.509	-0.534	-0.560	-0.588	-0.617
0.4002	-0.588	-0.611	-0.638	-0.667	-0.697	-0.729
0.4927	-0.621	-0.651	-0.679	-0.707	-0.738	-0.770
0.6003	-0.583	-0.604	-0.628	-0.651	-0.678	-0.705
0.6914	-0.424	-0.439	-0.458	-0.477	-0.498	-0.521
0.7963	-0.287	-0.296	-0.309	-0.322	-0.337	-0.353
0.9003	-0.165	-0.177	-0.184	-0.191	-0.199	-0.207
1.0000	0.000	0.000	0.000	0.000	0.000	0.000
X(ACN)			AN-ACN			
0.0000	0.000	0.000	0.000	0.000	0.000	0.000
0.1011	-0.006	-0.006	-0.006	-0.007	-0.005	-0.006
0.2065	-0.024	-0.024	-0.025	-0.025	-0.025	-0.025
0.3060	-0.023	-0.023	-0.024	-0.024	-0.023	-0.023
0.4002	-0.026	-0.026	-0.027	-0.026	-0.025	-0.025
0.5002	-0.026	-0.026	-0.027	-0.027	-0.026	-0.026
0.6010	-0.028	-0.028	-0.029	-0.029	-0.028	-0.028
0.7015	-0.029	-0.030	-0.030	-0.030	-0.030	-0.030
0.7980	-0.032	-0.012	-0.013	-0.016	-0.021	-0.010
0.8969	-0.028	-0.007	-0.024	-0.025	-0.028	-0.016
1.0000	0.000	0.000	0.000	0.000	0.000	0.000

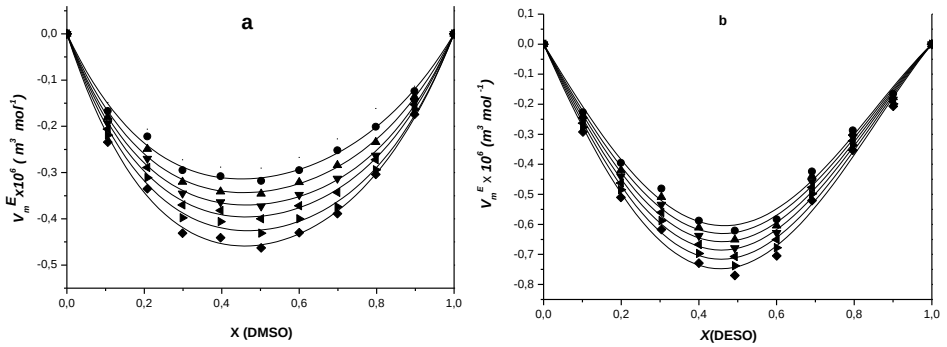


Fig. 1 Excess molar volumes, $V_m^E \times 10^6 \left(m^3 mol^{-1}\right)$, of binary solutions of AN at T=(298.15-323.15) *K*: (a) AN-DMSO; (b) AN-DESO, 298.15K (●); 303.15K (▲); 308.15K (▼); 313.15K (◄); 318.15K(►); 323.15K (◆).

As it was expected, deviations from the ideal behavior of AN-ACN mixture are negligible which is due to the fact that interactions between nitrile groups of identical and different molecules practically equivalent. As an illustration the dependences of V_m^E on molar fraction of tree solvents (DESO, DMSO, ACN) at temperature 298.15K are presented in Fig. 2.

Excess molar volumes were described by the Redlich–Kister polynomial equation [17, 18].

$$\mathrm{Y}^E = x_1\left(1-x_1\right)\sum_{i=0}^{m} A_i\left(2x_1-1\right)^i \qquad (2)$$

The Redlich–Kister coefficients, A_i, and standard deviations, σ, are summarized in Table 3. σ is evaluated from the equation

$$\sigma = \left[\sum\left(\mathrm{Y}^E_{\mathrm{expt}} - \mathrm{Y}^E_{\mathrm{calc}}\right)^2/\left(m-n\right)\right]^{1/2} , \qquad (3)$$

where *m* is the number of results and *n* is the number of parameters retained in equation (3).

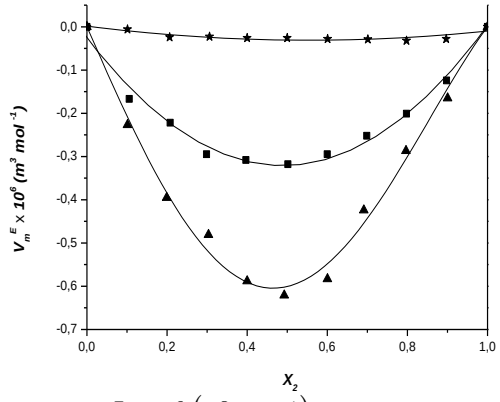


Fig. 2- Excess molar volumes, $V_m^E \times 10^6 \left(m^3 mol^{-1}\right)$, of binary solutions of AN at T=298.15K: (■) AN-DMSO; (▲) AN-DESO; (★) AN-ACN.

Table 3

Redlich-Kister fitting coefficients, A_i, and standard deviations, $\sigma\left(V_m^E \times 10^6 / m^3 mol^{-1}\right)$, of the excess molar volumes for the AN solutions in DMSO, DESO and ACN at temperatures from (298.15 to 323.15) K

T/K	A_0	A_1	A_2	$\sigma\left(V_m^E\right)$
		AN-DMSO		
298.15	-1.2459	0.1853	-0.3337	0.010
303.15	-1.3662	0.1686	-0.4337	0.008
308.15	-1.4749	0.1451	-0.5134	0.009
313.15	-1.5782	0.1585	-0.5152	0.010
318.15	-1.6977	0.1527	-0.5516	0.012
323.15	-1.8259	0.2223	-0.5206	0.011
		AN-DESO		
298.15	-2.4026	0.4409	0.7254	0.026
303.15	-2.5023	0.4977	0.7006	0.027
308.15	-2.6093	0.5356	0.7071	0.028
313.15	-2.7183	0.5808	0.7130	0.028
318.15	-2.8375	0.6226	0.7163	0.028
323.15	-2.9613	0.6682	0.7114	0.029
		AN-ACN		
298.15	-0.1052	-0.0622	-0.1524	0.004
303.15	-0.1164	0.0072	0.0302	0.004
308.15	-0.1128	-0.0166	-0.0543	0.006
313.15	-0.1106	-0.0235	-0.0787	0.005
318.15	-0.1058	-0.0426	-0.1119	0.005
323.15	-0.1113	-0.0013	-0.0144	0.005

As it follows from Fig. 3, V_m^E values for AN-DMSO binary mixtures are more negative than those for ACN-DMSO mixtures.

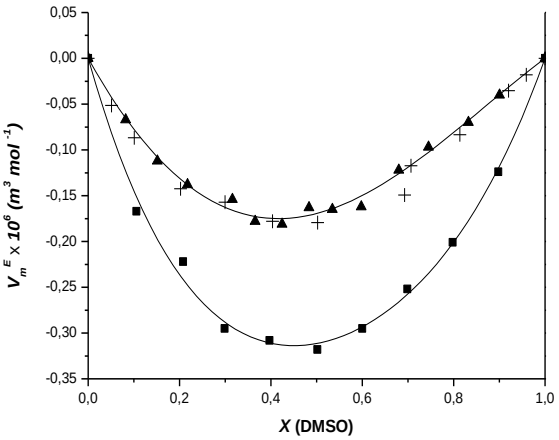


Fig. 3-Excess molar volumes, $V_m^E \times 10^6 \left(m^3 mol^{-1}\right)$, of binary solutions at T=298.15K: (■) AN-DMSO; (▲) ACN-DMSO (this work); (+) ACN-DMSO (ref. 5).

To explain this observation it should be mentioned that when groups such as $C \equiv N$ are adjacent to a multiple bond, they withdraw π electrons from multiple

bond through resonance or mesomeric effect. Obviously, such a type interaction occurs between *C*=*C* and $C \equiv N$ groups in AN molecules. As a result the polarity of $C \equiv N$ group in AN molecule is increasing and hence more strong interaction between $C \equiv N$ group of AN and *S*=*O* group of DMSO takes place.

Apparent and Partial Molar Volumes.

In a binary liquid mixture, the apparent molar volumes $V_{\phi,1}$ and $V_{\phi,2}$ of components 1 (AN) and 2 (DMSO or DESO) are calculated by following equations [18, 19]:

$$V_{\phi,1} = V_1^* + V_m^E / x_1 \quad \text{and } V_{\phi,2} = V_2^* + V_m^E / x_2 , \tag{4}$$

where V_1^* and V_2^* are the molar volume of pure AN and solvents (DMSO or DESO), respectively. The data for the above mentioned binary solutions at temperature from 298.15K to 323.15K are presented in Table 4a, b.

Table 4a

Apparent molar volumes ($V_{\phi,i}$), partial molar volumes ($\overline{V}_i$), and excess partial molar volumes ($\overline{V}_i^E$) of AN(1)-DMSO(2) binary solutions at T=(298.15-323.15) K

X_2	$V_{\phi,1}\times10^6$ $(m^3\ mol^{-1})$	$V_{\phi,1}\times10^6$ $(m^3\ mol^{-1})$	$\overline{V_1}\times10^6$ $(m^3\ mol^{-1})$	$\overline{V_2}\times10^6$ $(m^3\ mol^{-1})$	$\overline{V}_1^E\times10^6$ $(m^3\ mol^{-1})$	$\overline{V}_2^E\times10^6$ $(m^3\ mol^{-1})$
			T = 298.15K			
0.1056	66.073	69.730	66.140	70.028	0.120	1.283
0.2079	65.979	70.241	66.094	70.724	0.166	0.587
0.2988	65.838	70.323	65.998	70.911	0.261	0.400
0.3968	65.748	70.534	65.965	71.191	0.295	0.120
0.5016	65.622	70.677	65.907	71.369	0.353	-0.058
0.5999	65.522	70.819	65.869	71.507	0.391	-0.196
0.6986	65.423	70.950	65.807	71.591	0.453	-0.279
0.7976	65.266	71.059	65.635	71.591	0.625	-0.280
0.8979	65.045	71.173	65.304	71.506	0.955	-0.195
			T = 303.15K			
0.1056	66.528	69.942	66.672	70.288	0.057	1.354
0.2079	66.414	70.442	66.643	71.003	0.086	0.639
0.2988	66.272	70.571	66.558	71.256	0.171	0.386
0.3968	66.164	70.783	66.505	71.553	0.223	0.090
0.5016	66.035	70.953	66.438	71.771	0.291	-0.129
0.5999	65.925	71.106	66.378	71.929	0.351	-0.287
0.6986	65.787	71.236	66.263	72.012	0.466	-0.370
0.7976	65.574	71.349	66.017	72.002	0.712	-0.360
0.8979	65.393	71.490	65.699	71.904	1.030	-0.262

T＝308.15K

0.1056	66.993	70.148	67.196	70.530	0.012	1.442
0.2079	66.868	70.675	67.184	71.296	0.024	0.676
0.2988	66.716	70.817	67.097	71.577	0.110	0.395
0.3968	66.604	71.054	67.042	71.912	0.166	0.060
0.5016	66.459	71.228	66.951	72.147	0.257	-0.175
0.5999	66.339	71.393	66.872	72.324	0.336	-0.352
0.6986	66.171	71.524	66.717	72.411	0.491	-0.439
0.7976	65.908	71.642	66.406	72.394	0.802	-0.422
0.8979	65.780	71.810	66.121	72.290	1.087	-0.318

T＝313.15K

0.1056	67.467	70.354	67.685	70.750	0.012	1.552
0.2079	67.331	70.910	67.673	71.554	0.024	0.748
0.2988	67.169	71.063	67.582	71.851	0.114	0.451
0.3968	67.064	71.339	67.537	72.229	0.159	0.073
0.5016	66.893	71.503	67.423	72.453	0.274	-0.152
0.5999	66.767	71.681	67.335	72.642	0.361	-0.340
0.6986	66.557	71.810	67.135	72.721	0.562	-0.419
0.7976	66.353	71.961	66.876	72.731	0.820	-0.429
0.8979	66.201	72.132	66.556	72.622	1.141	-0.320

T＝318.15K

0.1056	67.950	70.560	68.203	70.981	-0.008	1.657
0.2079	67.803	71.142	68.198	71.827	-0.003	0.812
0.2988	67.627	71.305	68.102	72.144	0.093	0.495
0.3968	67.521	71.614	68.059	72.563	0.136	0.076
0.5016	67.330	71.779	67.921	72.794	0.274	-0.155
0.5999	67.195	71.972	67.821	72.999	0.374	-0.361
0.6986	66.953	72.103	67.581	73.079	0.615	-0.440
0.7976	66.740	72.269	67.303	73.096	0.893	-0.457
0.8979	66.598	72.457	66.977	72.983	1.219	-0.345

T＝323.15K

0.1056	68.444	70.760	68.707	71.198	-0.002	1.781
0.2079	68.283	71.369	68.703	72.080	0.003	0.899
0.2988	68.091	71.537	68.603	72.405	0.103	0.574
0.3968	67.975	71.868	68.560	72.843	0.146	0.135
0.5016	67.777	72.056	68.422	73.089	0.284	-0.111
0.5999	67.631	72.262	68.310	73.297	0.396	-0.318
0.6986	67.413	72.421	68.088	73.392	0.618	-0.414
0.7976	67.205	72.598	67.802	73.411	0.903	-0.433
0.8979	67.000	72.785	67.397	73.297	1.309	-0.319

Table 4b

Apparent molar volumes ($V_{\phi,i}$), partial molar volumes ($\bar{V}_i$), and excess partial molar volumes ($\bar{V}_i^E$) of AN(1)-DESO(2) binary solutions at T=(298.15-323.15) K

X_2	$V_{\phi,1}\times10^6$ $\left(m^3\ mol^{-1}\right)$	$V_{\phi,1}\times10^6$ $\left(m^3\ mol^{-1}\right)$	$\bar{V}_1\times10^6$ $\left(m^3\ mol^{-1}\right)$	$\bar{V}_2\times10^6$ $\left(m^3\ mol^{-1}\right)$	$\bar{V}_1^E\times10^6$ $\left(m^3\ mol^{-1}\right)$	$\bar{V}_2^E\times10^6$ $\left(m^3\ mol^{-1}\right)$
			T = 298.15K			
0.1014	66.003	102.473	65.702	102.511	0.554	2.205
0.1992	65.763	102.732	65.404	102.821	0.852	1.896
0.3033	65.566	103.131	65.289	103.241	0.967	1.475
0.4002	65.275	103.246	65.129	103.323	1.127	1.393
0.4927	65.033	103.456	65.010	103.450	1.247	1.266
0.6003	64.796	103.744	64.874	103.597	1.383	1.119
0.6914	64.881	104.102	64.991	103.831	1.265	0.885
0.7963	64.848	104.356	64.939	103.998	1.318	0.718
0.9003	64.602	104.533	64.640	104.235	1.617	0.481
			T = 303.15K			
0.1014	66.460	102.817	66.182	102.888	0.543	2.279
0.1992	66.201	103.059	65.881	103.199	0.844	1.967
0.3033	65.995	103.488	65.768	103.660	0.957	1.506
0.4002	65.707	103.640	65.619	103.782	1.106	1.384
0.4927	65.442	103.845	65.482	103.902	1.243	1.264
0.6003	65.214	104.160	65.356	104.071	1.369	1.095
0.6914	65.304	104.532	65.476	104.312	1.249	0.854
0.7963	65.274	104.795	65.417	104.477	1.309	0.690
0.9003	64.954	104.970	65.023	104.694	1.702	0.472
			T = 308.15K			
0.1014	66.925	103.148	66.651	103.235	0.554	2.387
0.1992	66.655	103.412	66.344	103.579	0.860	2.044
0.3033	66.438	103.861	66.229	104.065	0.976	1.557
0.4002	66.141	104.029	66.078	104.204	1.127	1.419
0.4927	65.866	104.245	65.936	104.333	1.268	1.290
0.6003	65.633	104.576	65.808	104.512	1.396	1.110
0.6914	65.721	104.960	65.925	104.758	1.280	0.864
0.7963	65.688	105.234	65.857	104.926	1.348	0.696
0.9003	65.362	105.418	65.447	105.146	1.757	0.476
			T = 313.15K			
0.1014	67.400	103.489	67.129	103.594	0.564	2.489
0.1992	67.115	103.763	66.815	103.959	0.877	2.123
0.3033	66.889	104.237	66.699	104.477	0.994	1.605
0.4002	66.581	104.417	66.544	104.628	1.148	1.455
0.4927	66.298	104.647	66.400	104.768	1.292	1.315
0.6003	66.063	104.997	66.274	104.959	1.419	1.123

0.6914	66.145	105.392	66.385	105.209	1.307	0.873
0.7963	66.111	105.678	66.310	105.380	1.382	0.703
0.9003	65.775	105.870	65.878	105.601	1.814	0.481
			T = 318.15K			
0.1014	67.883	103.816	67.619	103.941	0.573	2.608
0.1992	67.586	104.114	67.300	104.342	0.892	2.207
0.3033	67.348	104.611	67.181	104.889	1.011	1.660
0.4002	67.029	104.807	67.023	105.057	1.168	1.491
0.4927	66.736	105.050	66.875	105.209	1.316	1.340
0.6003	66.496	105.420	66.747	105.413	1.445	1.136
0.6914	66.577	105.828	66.855	105.669	1.337	0.880
0.7963	66.536	106.125	66.767	105.842	1.425	0.707
0.9003	66.195	106.328	66.317	106.065	1.875	0.484
			T = 323.15K			
0.1014	68.377	104.138	68.124	104.286	0.578	2.733
0.1992	68.066	104.460	67.803	104.727	0.899	2.292
0.3033	67.817	104.986	67.683	105.311	1.019	1.708
0.4002	67.487	105.197	67.522	105.497	1.180	1.522
0.4927	67.184	105.456	67.370	105.662	1.332	1.357
0.6003	66.937	105.844	67.238	105.879	1.464	1.140
0.6914	67.013	106.265	67.339	106.140	1.363	0.879
0.7963	66.970	106.576	67.241	106.316	1.461	0.703
0.9003	66.629	106.790	66.775	106.539	1.927	0.480

As it follows from presented data for AN-DMSO and AN-DESO mixtures with the increase of mole fractions of both components, the apparent molar volumes increase, but the temperature increasing leads to the decreasing apparent molar volumes. The same behavior is observed for partial molar volumes as well.

The partial molar volumes, $\overline{V}_i$, can be determined from excess molar volumes data using following equation:

$$\overline{V}_i = V_i^* + V^E / x_i + x_i(1-x_i)(\partial\left(V^E / x_i\right)/ \partial x_i)_{T,P}, \quad (5)$$

where $(\partial\left(V_m{}^E / x\right)/ \partial x_i)_{T,P}$ is calculated using Redlich–Kister polynomial equation (2) and V_i^* represent the molar volumes of the component 1 (AN) or 2 (DMSO; DESO).

Partial molar volumes at infinite dilution, V_i^∞, are considered of particular interest because of their usefulness in examining solute-solvent interactions, as solute-solute interactions can be assumed to be eliminated at infinite dilution.

The limiting partial molar volumes, V_i^∞, were estimated by extrapolating the apparent molar volumes to infinite dilution. The limiting partial molar volumes of AN and DMSO (or DESO) in binary mixtures at temperatures from 298.15K to 323.15K are given in Table 5.

Table 5

Limiting partial molar volumes (V_i^{∞}) of component of AN-DMSO and AN-DESO binary mixtures at temperatures from 298.15 to 323.15K

T/K	AN-DMSO	
	$V_{\phi}^{\infty}(AN)\times10^{6}$ $\left(m^3\ mol^{-1}\right)$	$V_{\phi}^{\infty}(DMSO)\times10^{6}$ $\left(m^3\ mol^{-1}\right)$
298.15	64.999	69.789
303.15	65.315	69.945
308.15	65.662	70.192
313.15	66.067	70.398
318.15	66.438	70.601
323.15	66.857	70.787
	AN-DESO	
	$V_{\phi}^{\infty}(AN)\times10^{6}$ $\left(m^3\ mol^{-1}\right)$	$V_{\phi}^{\infty}(DESO)\times10^{6}$ $\left(m^3\ mol^{-1}\right)$
298.15	64.297	102.255
303.15	64.675	102.578
308.15	65.068	102.906
313.15	65.468	103.237
318.15	65.872	103.560
323.15	66.285	103.879

As seen from data the infinite dilution values decrease with increasing temperature. Noteworthy is the item that at infinite dilution the partial molar volumes and apparent molar volumes of both AN and DMSO (or DESO) are equal and smaller than for the corresponding pure solvents. This also indicates the existence of interaction between these molecules.

The excess partial molar volumes, $\overline{V}_i^E$, of a component in a binary AN-DMSO and AN-DESO mixtures can be determined from the relation (6) and given in Table 4(a, b):

$$\overline{V}_i^E = V_i^* - \overline{V}_i . \tag{6}$$

For comparison, the corresponding data for AN-DMSO and AN-DESO binary mixtures at (298.15 and 318.15)K temperatures calculated by us are presented in Fig. 4.

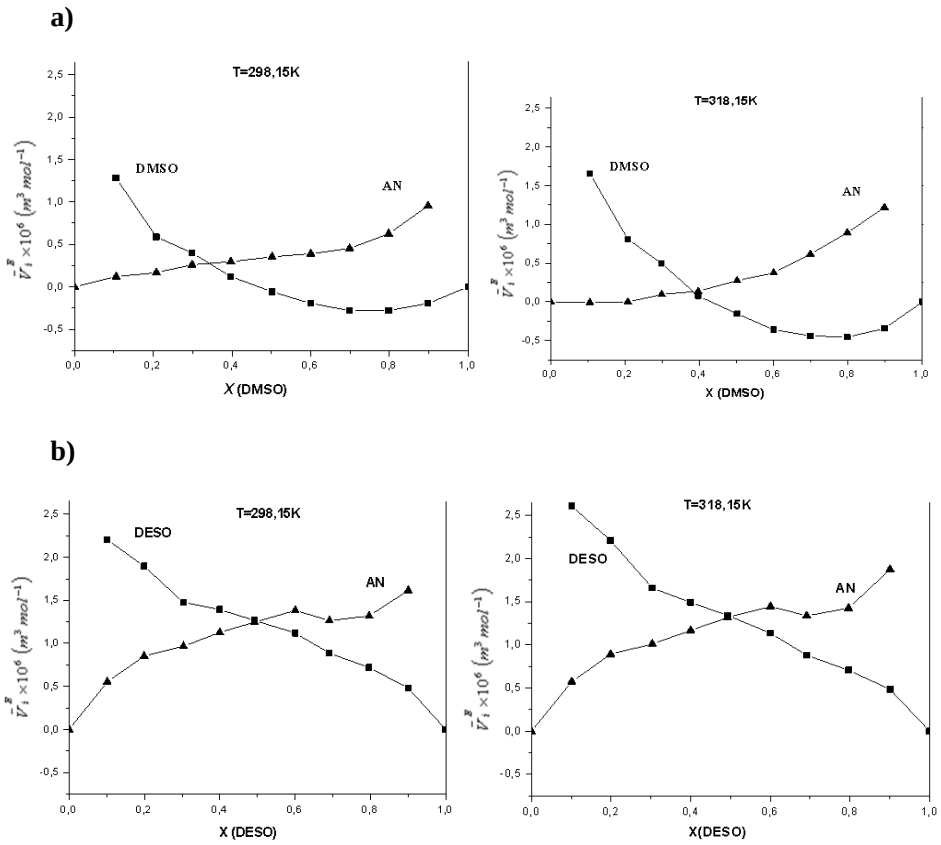


Fig. 4 Excess partial molar volumes, $\overline{V}_i^E \times 10^6 \left(m^3\, mol^{-1}\right)$, of components in binary solutions of AN at T = (298.15 and 318.15) K: (a) AN-DMSO; (b) AN-DESO.

Thermal Expansion Coefficients.

A commonly encountered derived value for mixtures is the temperature dependence of density that is expressed by thermal expansion coefficient. The thermal expansion coefficient, α_p, is given by the relation (7) and are presented in Table 6.

$$\alpha_p = (1/V)(\delta V/\delta T)_p = -(1/\rho)(\delta\rho/\delta T)_p, \qquad (7)$$

As follows from these data, the expansion coefficients against mole fraction of DMSO or DESO are monotone decrease.

Table 6

Cubic expansion coefficients (α) of mixtures of AN with DMSO and DESO at temperatures from (298.15 to 323.15) K

T/K	$\alpha \times 10^3 (K^{-1})$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
X(DMSO)			AN-DMSO			
0.0000	1.424	1.434	1.444	1.454	1.465	1.476
0.1056	1.328	1.336	1.345	1.354	1.364	1.373
0.2079	1.255	1.263	1.271	1.279	1.287	1.296
0.2988	1.192	1.199	1.207	1.214	1.222	1.229
0.3968	1.143	1.150	1.156	1.163	1.170	1.177
0.5016	1.085	1.091	1.097	1.103	1.109	1.115
0.5999	1.044	1.049	1.054	1.060	1.066	1.071
0.6986	0.975	0.980	0.985	0.990	0.995	1.000
0.7976	0.940	0.945	0.949	0.954	0.958	0.963
0.8979	0.935	0.940	0.944	0.949	0.953	0.958
1.0000	0.913	0.917	0.921	0.925	0.930	0.934
X(DESO)			AN-DESO			
0.0000	1.424	1.434	1.444	1.454	1.465	1.476
0.1014	1.304	1.313	1.321	1.330	1.339	1.348
0.1992	1.213	1.220	1.228	1.235	1.243	1.251
0.3033	1.142	1.148	1.155	1.162	1.168	1.175
0.4002	1.080	1.086	1.092	1.098	1.104	1.110
0.4927	1.025	1.030	1.035	1.041	1.046	1.052
0.6003	0.982	0.987	0.992	0.997	1.002	1.007
0.6914	0.947	0.952	0.956	0.961	0.965	0.970
0.7963	0.912	0.916	0.920	0.924	0.929	0.933
0.9003	0.889	0.892	0.896	0.900	0.904	0.909
1.0000	0.858	0.862	0.865	0.869	0.873	0.877

Conclusions

The excess molar volumes exhibit negative deviations from the ideal behavior over the whole range of composition and temperature for AN-DMSO and AN-DESO mixtures and become more negative with increasing temperature from 298.15 to 323.15K. The results are interpreted on the basis of dipole-dipole interaction between polar $C \equiv N$ and $S = O$ groups.

More negative values of V_m^E in AN-DMSO mixture compare to ACN-DMSO, one can explain on the basis of conjugation between $C = C$ and $C \equiv N$ groups of AN which results in the increasing of polarity of $C \equiv N$ group due to electron withdrawing resonance effect.

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ԴԻՄԵԹԻԼՍՈՒԼՖՕՔՍԻԴԻ ԵՎ ԴԻԷԹԻԼՍՈՒԼՖՕՔՍԻԴԻ ՀԵՏ ԱԿՐԻԼՈՆԻՏՐԻԼԻ ԲԻՆԱՐ ԽԱՌՆՈՒՐԴՆԵՐԻ ԾԱՎԱԼԱՅԻՆ ՀԱՏԿՈՒԹՅՈՒՆՆԵՐԸ 298.15-323.15 Կ ՋԵՐՄԱՍՏԻՃԱՆԱՅԻՆ ՏԻՐՈՒՅԹՈՒՄ

Ե. Ա. ՂԱԶՈՅԱՆ, Զ. Լ. ԳՐԻԳՈՐՅԱՆ և Շ. Ա. ՄԱՐԳԱՐՅԱՆ

Չափվել են ակրիլոնիտրիլի բինար լուծույթների խտությունները ապրոտիկ բևեռային լուծիչներ հանդիսացող դիմեթիլ- և դիէթիլսուլֆօքսիդներում ամբողջ կոնցենտրացիոն տիրույթում 298.15-ից 323.15 Կ ջերմաստիճաններում: Հաշվարկվել են այդ հեղուկ խառնուրդների հավելյալ, թվացյալ, պարցիալ, հավելյալ պարցիալ և անսահման նոսրացման պարցիալ մոլային ծավալները, ինչպես նաև ջերմային ընդարձակման գործակիցները: Հավելյալ մոլային ծավալները ամբողջ կոնցենտրացիոն տիրույթում ստացվել են բացասական և ջերմաստիճանի մեծացման հետ դրանց բացասական արժեքները ավելի են մեծանում: Հավելյալ մոլային ծավալների արժեքները համապատասխանեցվել են Ռեդլիխ-Կիստերի հավասարմամբ: Ստացված արդյունքները մեկնաբանվում են հիմնվելով ակրիլոնիտրիլի նիտրիլ և սուլֆօքսիդների S=O խմբերի միջև դիպոլ-դիպոլային փոխազդեցության վրա:

ОБЪЕМНЫЕ СВОЙСТВА БИНАРНЫХ РАСТВОРОВ АКРИЛОНИТРИЛА В ДИМЕТИЛ- И ДИЭТИЛСУЛЬФОКСИДАХ В ТЕМПЕРАТУРНОМ ИНТЕРВАЛЕ 298.15 - 323.15К

Е. А. КАЗОЯН, З. Л. ГРИГОРЯН и Ш. А. МАРКАРЯН

Измерены плотности бинарных растворов акрилонитрила в таких апротонных полярных растворителях, как диметил- и диэтилсульфоксиды во всем концентрационном диапазоне и в температурном интервале 298.15-323.15К. Рассчитаны избыточные мольные объемы, кажущиеся мольные объемы, парциальные мольные объемы, парциальные избыточные мольные объемы и коэффициенты термического расширения бинарных растворов. Величины избыточных мольных объемов отрицательны во всем концентрационном диапазоне и с ростом температуры отрицательные отклонения увеличиваются. Избыточные мольные объемы описаны уравнением Редлиха-Кистера. Полученные результаты обсуждаются на основе диполь-дипольного взаимодействия между нитрильной группой акрилонитрила и S=O группами сульфоксидов.

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