Refractivity and density of some organic solvents

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Dedicated to Associate Professor K. Matiašovský, DrSc., in honour of his 60th birthday

Densities and refractive indices of hexamethylphosphoric triamide, *N*-methylacetamide, *N*,*N*-dimethylacetamide, dioxane, acetonitrile, formamide, *N*-methylformamide, and methanol were measured at various temperatures. Polarizabilities and molecular radii were calculated and compared with the values evaluated from the molar volume of the liquids and from geometrical considerations.

Density, refractive index, and molar volume of the solvent are valuable parameters for description of the behaviours of electrolyte solutions and for investigation of the solvation effects. This work presents new aspects of the molecular properties of hexamethylphosphoric triamide (HMPT), *N*-methylacetamide (NMA), *N*,*N*-dimethylacetamide (DMA), dioxane, acetonitrile (AN), formamide (FA), *N*-methylformamide (NMF), and methanol (MeOH) derived from new measurements of refractive indices and densities and from previously published data [1].

Experimental

The organic solvents (anal. grade, Merck) containing less than 0.1 % of water were used as received. Any traces of impurities and water present in the solvent do not affect the density and refractive index values as it was experimentally verified.

Density was measured by means of digital densimeter DMA 40 (Paar, Austria) with an accuracy better than $\pm 4 \times 10^{-4}$ g cm^{-3} Refractive indices were determined at a wavelength 587.6 nm (He, D-line) with an accuracy of $\pm 5 \times 10^{-5}$ The measurements were performed at temperatures maintained with the accuracy ± 0.05 °C in the region from 10 to 60 °C.

Results and discussion

The experimental values of densities and refractive indices are given in Table 1 together with calculated values of molar volumes and molar refractions.

Table 1

Experimental values of densities ϱ and indices of refraction n and calculated values of molar volumes V_m and molar refractions $[R]$ in dependence on temperature

θ/°C	ϱ / g cm^{-3}	V_m / cm^3 mol^{-1}	n	$[R]$ / cm^3 mol^{-1}	θ/°C	ϱ / g cm^{-3}	V_m / cm^3 mol^{-1}	n	$[R]$ / cm^3 mol^{-1}
	Hexamethylphosphoric triamide (HMPT)					Formamide (FA)			
10	1.0340	173.31	1.46299	47.73	10	1.1412	39.47	1.45071	10.62
20	1.0247	174.87	1.45898	47.81	20	1.1333	39.74	1.44735	10.63
30	1.0162	176.34	1.45507	47.85	30	1.1249	40.04	1.44390	10.63
40	1.0078	177.81	1.45120	47.90	40	1.1164	40.34	1.44060	10.65
50	0.9991	179.36	1.44723	47.94	50	1.1080	40.65	1.43698	10.65
60	0.9906	180.90	1.44319	47.98	60	1.0991	40.98	1.43330	10.66
	N-Methylacetamide (NMA)					*N*-Methylformamide (NMF)			
30	0.9502	76.93	1.42916	19.86	10	1.0128	58.32	1.43605	15.25
35	0.9462	77.26	1.42723	19.84	20	1.0038	58.85	1.43236	15.27
40	0.9420	77.60	1.42532	19.86	30	0.9951	59.36	1.42854	15.29
50	0.9335	78.30	1.42141	19.87	40	0.9865	59.88	1.42453	15.30
60	0.9251	79.02	1.41749	19.89	50	0.9776	60.42	1.42085	15.32
65	0.9210	79.37	1.41557	19.90	60	0.9689	60.97	1.41699	15.33

Table 1 (Continued)

θ/°C	ϱ / g cm^{-3}	V_m / cm^3 mol^{-1}	n	$[R]$ / cm^3 mol^{-1}	θ/°C	ϱ / g cm^{-3}	V_m / cm^3 mol^{-1}	n	$[R]$ / cm^3 mol^{-1}
	N,*N*-Dimethylacetamide (DMA)					Dioxane			
10	0.9502	91.69	1.44237	24.28	10	1.0447	84.34	1.42687	21.65
20	0.9409	92.59	1.43815	24.31	20	1.0336	85.25	1.42207	21.67
30	0.9317	93.51	1.43374	24.34	30	1.0224	86.18	1.41754	21.70
40	0.9228	94.41	1.42945	24.36	40	1.0112	87.13	1.41284	21.72
50	0.9134	95.38	1.42509	24.39	50	0.9997	88.14	1.40815	21.75
60	0.9040	96.37	1.42074	24.43	60	0.9881	89.17	1.40352	21.79
	Acetonitrile (AN)					Methanol (MeOH)			
5	0.7995	51.34	1.35083	11.07	5	0.8056	39.77	1.33425	8.21
10	0.7995	51.67	1.34869	11.08	10	0.8010	40.00	1.33223	8.21
15	0.7883	52.07	1.34619	11.09	15	0.7962	40.24	1.33018	8.21
20	0.7821	52.49	1.34367	11.11	20	0.7916	40.48	1.32837	8.22
25	0.7767	52.85	1.34140	11.12	25	0.7868	40.72	1.32637	8.22
30	0.7714	53.21	1.33892	11.12	30	0.7822	40.96	1.32443	8.23
35	0.7660	53.59	1.33630	11.12	40	0.7729	41.45	1.32058	8.24
40	0.7606	53.97	1.33411	11.13					

Both the densities ϱ and the refractive indices n show linear temperature dependences from 10 to 60 °C and these have been fitted to the equations

$$\varrho = A - B\theta \tag{1}$$

$$n = C - D\theta \tag{2}$$

The coefficients A, B for density and C, D for refractive index are presented in Table 2.

Table 2

Coefficients A, B of the density—temperature dependence and C, D of the refractive index—temperature (at $\lambda = 587.6$ nm) dependence (eqns (*1* and *2*))

Solvent	A	B 10^4	10^4	C	D 10^4	10^5
HMPT	1.0423	8.63	2.61	1.46692	3.95	5.32
NMA	0.9754	8.38	0.87	1.44085	3.81	2.15
DMA	0.9594	9.21	1.51	1.44675	4.33	4.38
AN	0.8051	11.21	4.06	1.35339	4.84	10.11
FA	1.1500	8.43	2.90	1.45429	3.47	13.00
NMF	1.0215	8.76	1.05	1.43994	3.82	8.37
DMF [1]	0.9678	9.49	0.90	1.43966	4.44	0.52
Dioxane	1.0562	11.31	2.07	1.43149	4.66	5.65
MeOH	0.8103	9.36	0.67	1.33613	3.90	6.10

On the basis of the Lorentz—Lorenz (LL) equation

$$[R] = \frac{n^2 - 1}{n^2 + 2} V_m = (4/3)\pi N_A \alpha_{LL} \tag{3}$$

the molar refraction $[R]$ and polarizability α_{LL} were calculated. V_m is the molar volume of the liquid and N_A is Avogadro's constant. Both $[R]$ and α_{LL} show a slight variation with temperature. Their values for $\lambda = 587.6$ nm and 30 °C are given in Table 3.

Bottcher [2] derived an improved relationship between the refractive index, polarizability α_B and the radius r_B of a spherical cavity surrounded by an otherwise continuous medium.

$$\frac{12\pi n^2}{(n^2 - 1)(2n^2 + 1)} \frac{N_A}{V_m} = \frac{1}{\alpha_B} - \frac{1}{r_B} \frac{(2n^2 - 2)}{(2n^2 + 1)} \tag{4}$$

By plotting the quantity on the left-hand side of eqn (*4*) against $(2n^2 - 2)/(2n^2 + 1)$ a straight line is obtained as n varies with temperature, α_B and r_B were

Table 3

Molar refraction [R], polarizability α_{LL} (eqn (*3*)), α_B and r_B (eqn (*4*)), apparent radius r, actual radius R, and free molar volume V_f° (calculated from geometrical considerations)

Solvent	[R]	α_{LL} [a]	α_B	r_B		R [a]	V_f°
	$cm^3\ mol^{-1}$	Å^3	Å^3	Å	Å	Å	cm^3
HMPT	47.9	18.98	19.1	4.2	4.12	3.70	47.9
NMA	19.8	7.87	7.9	3.1	3.12	2.81	21.0
DMA	24.3	9.65	9.8	3.5	3.33	3.00	25.8
AN	11.1	4.41	—	—	2.76	2.48	14.6
FA	10.6	4.21	4.1	2.4	2.51	2.26	11.0
NMF	15.3	6.06	6.0	2.8	2.87	2.57	16.2
DMF [1]	20.0	8.00	7.9	3.1	3.13	2.81	21.2
Dioxane	21.7	8.61	8.8	3.5	3.24	2.92	23.8
MeOH	8.2	3.26	3.3	2.9	2.53	2.27	11.2
DMSO [1]	20.2	8.00	8.3	3.4	3.05	2.73	19.4
Water [3]	3.7	1.47	1.3	1.4	1.93	1.73	4.9

a) The values were calculated from the experimental values of n and V_m at 30 °C. Estimated errors in all values are ±1 of the last digit quoted.

calculated from the slope and intercept of the plot and their values are given in Table 3 together with the values for water taken from Ref. [3] and for dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF) taken from Ref. [1]. It should be noted that the data for AN do not fit eqn (*4*) so that r_B and α_B cannot be estimated. (Probably because the AN molecule has linear chain structure and not spherical one.)

The polarizabilities calculated from eqn (*3*) are close to those predicted from the Bottcher equation. The Bottcher's values of r_B were compared with the apparent radii r of the molecules calculated from the molar volume of the liquid

$$V_m = M/\varrho = (4/3)\pi N_A r^3 \qquad (5)$$

where M is the molar mass. In this case it is assumed that molecules are spherical and no void volume in the liquid is taken into account and the actual radius of molecules should be therefore smaller. The void volume around the liquid molecules can be derived on the basis of geometrical consideration the details of which are given in Ref. [4]. If a molecule of the liquid of radius R is surrounded by 12 other molecules of the same radius, the void (free) molar volume V_f° is

$$V_f^\circ = 1.59R^3N_A \qquad (6)$$

The actual molecular radius R was calculated from the relationship between V_m and actual molar volume $V°$

$$V_m = V° + V_f° \tag{7}$$

where $V° = (4/3)\pi N_A R^3$. The values of R are given in Table 3.

The molar refraction $[R]$ reflects arrangement of the electron shells of ions in molecules. It is a measure of polarizability or deformability of molecules. The higher the value of $[R]$ the greater and more deformable molecule is. Increase in the $[R]$ values can be observed in the order FA, NMF, DMF; and NMA, DMA (Table 3) as the size of the molecules increases.

The molar refraction has a dimension of molar volume. On the basis of comparison between the experimental values of $[R]$ and the void volume calculated from geometrical considerations (Table 3) it seems that the molar refraction can be regarded as the free molar volume which affects the deformability of the molecules. Water and methanol do not fit well to this theory, probably due to the formation of hydrogen bonds in these solvents.

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