Density and Volumic Properties of *N*,*N*-Dimethylformamide +2-Methoxyethanol+1,2-Dimethoxyethane Liquid Ternary Mixtures

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Densities (ρ) at various temperatures ranging from −10 up to +80 °C have been measured for *N*,*N*-dimethylformamide+2-methoxyethanol+1,2-dimethoxyethane ternary solvent system, employing 66 mixtures covering the whole miscibility field. Polynomial equations describing the dependence on temperature, $\rho=\rho(t/°C)$, and molar composition, $\rho=\rho(X_1,X_2)$, have been checked. Furthermore, the excess molar volumes (V^E), derived from ρ values, can provide useful suggestions about the formation of solvent–cosolvent complexes. Excess molar volumes have been interpreted on the basis of specific interactions between unlike molecules, taking into account geometric effects and steric hindrances. The V^E quantities have been isothermally fitted by an empirical relation of the type $V^E=V^E(X_1,X_2,X_3)$ formally derived from the well known Redlich–Kister equation. As a rule, for all the here tested relationships, the calculated values agree very well with the experimental ones, indicating that all the equations can be safely employed for predictive calculations in correspondence of the experimental data gaps.

In recent years noticeable importance has been given to the behavior of electrolytic and nonelectrolytic solutions in different nonaqueous solvents, because of their wide employment in industrial processes (polymers solvents, painting and varnishes, galvano-technique, etc.) and in electroanalytical studies.

Density and related properties, such as excess molar volumes, have been extensively studied for binary mixtures from both theoretical and experimental points of view.[1,2] However, experimental data and investigations on volumetric behavior of mixtures containing more than two components are quite scarce in the literature.[3] So, it seems useful to derive the excess molar volume and to attempt some interpretations of the results for ternary mixtures.

For this paper we have chosen *N*,*N*-dimethylformamide (DMF, component 1), 2-methoxyethanol (ME, component 2), and 1,2-dimethoxyethane (DME, component 3) as pure species and 63 ternary mixtures of theirs covering the whole miscibility range expressed by the relation $0\leq X_1/X_2/X_3\leq 1$. The above mentioned pure solvents and their binary mixtures were largely investigated in our previous works, either for electroanalytical or thermomechanical studies.[4—9]

Experimental

Materials. The solvents DMF, ME, and DME (containing< 0.10%, <0.05%, and <0.10% by mass of water, respectively, found by Karl–Fischer titrations) were high-purity-grade reagents from Carlo Erba (Milan). DMF and ME were purified by passage through a neutral alumina column. DME was further purified by double fractional distillation over $LiAlH_4$ to eliminate the traces of acids and peroxides and to reduce the total amount of water, keeping the middle fraction only (bp 83 °C) for the measurements. All the purified solvents were preserved over 3 Å type molecular sieves for many days before use. The final purity was checked by gas chromatography (99.8% for DMF, 99.7% for ME and DME), confirming the absence of other significant organic components.

Apparatus and Procedures. All binary and ternary mixtures were prepared, just before use, by weight on a Mettler PM 4800 Δ-range balance, operating in a dry box to avoid the atmospheric moisture. The probable error in each mole fraction X_i is estimated to be less than 1.5×10^{-4}. The apparatus, procedures and experimental details for the density measurements have been described elsewhere.[6]

Results and Discussion

In the present work we have measured the densities (ρ) of the DMF(1)+ME(2)+DME(3) solvent system at 19 temperatures in the $-10\leq t/°C\leq+80$ range, with thermal scanning of 5 °C, for 36 ternary mixtures covering the whole composition range expressed by the mole fraction X_i ($0<X_i<1$). The densities of pure components and their binaries DMF/ME,[6] ME/DME,[8] and DMF/DME[9] have been taken from our previous papers. The experimental ternary density data are listed in Table 1, together with the ternary composition of the mixtures.

At first, it should be noted that the trend of the inves-

Table 1. Ternary Composition and Experimental Density Values (ρ/g cm^{-3}) for DMF(1)/ME(2)/DME(3) Mixtures at Various Temperatures

(1)

	X_1	0.8209	0.7206	0.7361	0.6115	0.6336	0.6372	0.5203	0.5323	0.5410	0.5608	0.4139	0.4244
	X_2	0.1009	0.2006	0.1071	0.3107	0.2085	0.1122	0.4027	0.3078	0.2143	0.1112	0.5099	0.4142
t/°C	X_3	0.0782	0.0788	0.1568	0.0778	0.1579	0.2506	0.0770	0.1599	0.2447	0.3280	0.0762	0.1614
−10		0.971691	0.973501	0.965118	0.975852	0.966833	0.957655	0.977160	0.968194	0.959547	0.951351	0.979124	0.969914
−5		0.967131	0.969008	0.960580	0.971352	0.962342	0.953033	0.972729	0.963705	0.955045	0.946786	0.974513	0.965267
0		0.962630	0.964462	0.955964	0.966768	0.957832	0.948286	0.968172	0.959205	0.950432	0.942090	0.969955	0.960705
5		0.957992	0.959847	0.951332	0.962189	0.953155	0.943618	0.963587	0.954588	0.945692	0.937387	0.965431	0.955998
10		0.953424	0.955199	0.946619	0.957543	0.948560	0.938836	0.958899	0.949868	0.941037	0.932713	0.960842	0.951378
15		0.948731	0.950553	0.941977	0.952963	0.943793	0.934135	0.954306	0.945237	0.936223	0.927945	0.956162	0.946657
20		0.944071	0.945923	0.937285	0.948322	0.939078	0.929356	0.949633	0.940523	0.931502	0.923080	0.951523	0.941999
25		0.939442	0.941257	0.932511	0.943602	0.934405	0.924589	0.944909	0.935751	0.926638	0.918313	0.946921	0.937243
30		0.934723	0.936588	0.927778	0.938927	0.929659	0.919792	0.940223	0.931015	0.921812	0.913374	0.942188	0.932514
35		0.929940	0.931846	0.923040	0.934274	0.924852	0.915009	0.935585	0.926339	0.917040	0.908531	0.937531	0.927848
40		0.925250	0.927161	0.918337	0.929558	0.920103	0.910132	0.930904	0.921593	0.912178	0.903544	0.932808	0.923095
45		0.920480	0.922401	0.913567	0.924762	0.915378	0.905269	0.926173	0.916757	0.907258	0.898630	0.928053	0.918266
50		0.915623	0.917565	0.908766	0.920018	0.910611	0.900393	0.921429	0.912028	0.902413	0.893637	0.923220	0.913515
55		0.910847	0.912767	0.903909	0.915223	0.905793	0.895549	0.916597	0.907200	0.897452	0.888527	0.918485	0.908615
60		0.905921	0.907849	0.899057	0.910308	0.900908	0.890589	0.911779	0.902287	0.892497	0.883455	0.913650	0.903734
65		0.901006	0.902934	0.894253	0.905472	0.896030	0.885570	0.906965	0.897398	0.887573	0.878383	0.908765	0.898877
70		0.896141	0.898018	0.889355	0.900543	0.891154	0.880416	0.902018	0.392350	0.882511	0.873215	0.903888	0.893888
75		0.891163	0.892984	0.884354	0.895485	0.886146	0.875226	0.896918	0.887282	0.877357	0.867925	0.899012	0.888859
80		0.886065	0.887850	0.879421	0.890478	0.880984	0.869990	0.891818	0.882004	0.872215	0.862711	0.894161	0.883694

(2)

	X_1	0.4348	0.4488	0.4614	0.3116	0.3199	0.3276	0.3363	0.3476	0.3921	0.2088	0.2128	0.2187
	X_2	0.3232	0.2191	0.1118	0.6106	0.5216	0.4271	0.3311	0.2230	0.1286	0.7129	0.6253	0.5380
t/°C	X_3	0.2420	0.3321	0.4268	0.0778	0.1585	0.2453	0.3326	0.4294	0.4793	0.0783	0.1619	0.2433
−10		0.961813	0.952402	0.943345	0.979795	0.971566	0.963132	0.954215	0.944269	0.939388	0.980919	0.972320	0.964070
−5		0.957154	0.947864	0.938610	0.975477	0.967060	0.958491	0.949472	0.939597	0.934672	0.976679	0.967808	0.959488
0		0.952443	0.943193	0.933887	0.971108	0.962564	0.953815	0.944751	0.934874	0.929875	0.972324	0.963325	0.954836
5		0.947701	0.938487	0.929040	0.966608	0.957983	0.949073	0.939953	0.930092	0.925023	0.967832	0.958757	0.950120
10		0.942981	0.933664	0.924263	0.962004	0.953307	0.944341	0.935088	0.925312	0.920103	0.963193	0.954098	0.945403
15		0.938265	0.928857	0.919346	0.957404	0.948647	0.939599	0.930283	0.920450	0.915215	0.958548	0.949456	0.940683
20		0.933525	0.924072	0.914496	0.952815	0.943964	0.934863	0.925394	0.915588	0.910316	0.953879	0.944796	0.935934
25		0.928774	0.919168	0.909538	0.948117	0.939304	0.930132	0.920579	0.910739	0.905320	0.949242	0.940136	0.931192
30		0.924041	0.914337	0.904665	0.943509	0.934552	0.925345	0.915675	0.905823	0.900394	0.944566	0.935405	0.926398
35		0.919207	0.909453	0.899661	0.938781	0.929756	0.920468	0.910793	0.900857	0.895375	0.939836	0.930605	0.921546
40		0.914365	0.904520	0.894676	0.934132	0.925000	0.915656	0.905923	0.895875	0.890358	0.935193	0.925852	0.916631
45		0.909421	0.899542	0.889723	0.929404	0.920131	0.910763	0.900976	0.890795	0.885240	0.930458	0.920991	0.911791
50		0.904478	0.894579	0.884672	0.924645	0.915258	0.905792	0.896020	0.885724	0.880164	0.925795	0.916136	0.906817
55		0.899567	0.889626	0.879597	0.919820	0.910380	0.900897	0.891067	0.880674	0.875066	0.921055	0.911281	0.901838
60		0.894549	0.884548	0.874429	0.914953	0.905504	0.895852	0.885981	0.875497	0.869897	0.916202	0.906293	0.896828
65		0.889440	0.879394	0.869261	0.909999	0.900539	0.890829	0.880893	0.870324	0.864645	0.911306	0.901334	0.891812
70		0.884331	0.874191	0.864084	0.905004	0.895529	0.885826	0.875692	0.865180	0.859399	0.906320	0.896351	0.886709
75		0.879235	0.868943	0.858749	0.899791	0.890454	0.880757	0.870340	0.859953	0.854058	0.901138	0.891282	0.881507
80		0.874001	0.863475	0.853446	0.894380	0.885387	0.875598	0.864941	0.854630	0.848602	0.895705	0.886114	0.876328

(3)

	X_1	0.2264	0.2349	0.2413	0.2458	0.1057	0.1076	0.1104	0.1120	0.1172	0.1183	0.1238	0.1283
	X_2	0.4391	0.3395	0.2311	0.1188	0.8158	0.7303	0.6452	0.5559	0.4523	0.3502	0.2394	0.1242
t/°C	X_3	0.3345	0.4256	0.5276	0.6354	0.0785	0.1621	0.2444	0.3321	0.4305	0.5315	0.6368	0.7475
−10		0.955118	0.945638	0.937137	0.928321	0.981963	0.973339	0.964943	0.951798	0.946273	0.937131	0.927306	0.918059
−5		0.950331	0.940887	0.932184	0.923191	0.977386	0.968696	0.960252	0.946970	0.941784	0.932222	0.922467	0.913188
0		0.945480	0.936142	0.927276	0.918100	0.972766	0.964103	0.955512	0.942158	0.937175	0.927292	0.917651	0.908253
5		0.940736	0.931432	0.922307	0.912955	0.968298	0.959514	0.950790	0.937386	0.932444	0.922469	0.912757	0.903305
10		0.935948	0.926645	0.917293	0.907770	0.963735	0.954867	0.946108	0.932547	0.927678	0.917556	0.907789	0.898311
15		0.931098	0.921778	0.912277	0.902622	0.959284	0.950241	0.941356	0.927646	0.922842	0.912706	0.902816	0.893304
20		0.926289	0.916996	0.907273	0.897472	0.954735	0.945606	0.936604	0.922794	0.917992	0.907745	0.897849	0.888208
25		0.921495	0.912091	0.902293	0.892372	0.950189	0.940972	0.931794	0.917915	0.913065	0.902790	0.892796	0.883067
30		0.916642	0.907204	0.897249	0.887180	0.945627	0.936283	0.927018	0.913056	0.908045	0.897763	0.887654	0.877854
35		0.911763	0.902286	0.892178	0.882060	0.941072	0.931495	0.922255	0.908148	0.903074	0.892714	0.882546	0.872675
40		0.906808	0.897373	0.887098	0.876898	0.936414	0.926714	0.917433	0.903149	0.898034	0.887602	0.877362	0.867414
45		0.901909	0.892354	0.881929	0.871699	0.931705	0.921910	0.912578	0.898167	0.892914	0.882403	0.872109	0.862097
50		0.896869	0.887219	0.876771	0.866438	0.926895	0.917103	0.907656	0.893144	0.887744	0.877141	0.866789	0.856755
55		0.891888	0.882099	0.871632	0.861224	0.922072	0.912227	0.902783	0.888106	0.882583	0.871901	0.861493	0.851405
60		0.886825	0.876820	0.866403	0.855863	0.917236	0.907288	0.897829	0.882964	0.877388	0.866647	0.856093	0.846051
65		0.881704	0.871382	0.861057	0.850539	0.912283	0.902380	0.892767	0.877768	0.872060	0.861389	0.850664	0.840611
70		0.876506	0.865867	0.855703	0.845071	0.907276	0.897507	0.887721	0.872428	0.866706	0.856122	0.845239	0.835133
75		0.871316	0.860135	0.850344	0.839472	0.902190	0.892540	0.882660	0.867028	0.861336	0.850990	0.839701	0.829700
80		0.866116	0.854173	0.844815	0.833843	0.897131	0.887693	0.877448	0.861561	0.855794	0.845892	0.834195	0.824167

tigated property is quite regular, the ρ values always decreasing as temperature increases. In many reports, the dependence of density on temperature (t/°C) is stated on the basis of a high power polynomial of the type[10]

$$\rho(t) = \sum_{0}^{h} a_h t^h, \quad (1)$$

where a_h (for h=0,1,2,3,4) are the adjustable parameters summarized in Table 2 along with the standard error of determination $\sigma(\rho)$. For the sake of completeness, we notice that the overall average uncertainties along the text will be referred to all 1254 (N) experimental density values including pure species, binary mixtures previously published and ternary mixtures of this work. On this basis, the goodness of the fitting Eq. 1 is ascertained by an average deviation $\overline{\Delta\rho}$=±0.000025 g cm^{-3}, evaluated by means of the equation

$$\overline{\Delta\rho} = \frac{1}{N}\sum_{N} |\rho_{\text{exptl}} - \rho_{\text{calcd}}|. \quad (2)$$

In order to investigate the variation of ρ with ternary composition, a literature survey provides very few studies about this problem; however, starting from the relationship

$$\rho(X_1) = \sum_{0}^{j} b_j X_1^j \quad (3)$$

which is commonly employed for binary liquid systems, we have tried to extend its availability to the ternary mixtures too. Therefore, the following equation was utilized to fit each isothermal data set, taking into account also the previously published data about binary mixtures in order to provide a more general overview:

$$\rho(X_1, X_2) = \sum_{0}^{j}\sum_{0}^{k} b_{jk} X_1^j X_2^k \quad (4)$$

whose b_{jk} coefficients ($0 \le j,k \le 4$), evaluated by the ordinary least-squares method,[11] are summarized in Table 3 along with the standard error of determination at each selected temperature. Equation 4 simulates the experimental values within $\overline{\Delta\rho}$=±0.00036 g cm^{-3}.

Table 2. Composition (X_i) and Coefficients a_h of Eq. 1 for DMF(1)/ME(2)/DME(3) Ternary Mixtures

X_1	X_2	X_3	a_0	$10^4 a_1$	$10^7 a_2$	$10^{11} a_3$	$10^{12} a_4$	$10^5 \sigma(\rho)$
0.8209	0.1009	0.0782	0.962597	−9.14782	−5.67184	345.340	−35.7262	3.3
0.7206	0.2006	0.0788	0.964424	−9.15826	−4.94825	430.478	−57.0615	2.8
0.7361	0.1071	0.1568	0.955956	−9.24964	−6.25255	802.291	−65.0310	3.0
0.6115	0.3107	0.0778	0.966767	−9.15130	−4.68013	386.182	−50.7460	2.8
0.6336	0.2085	0.1579	0.957800	−9.17803	−12.2134	2229.58	−170.238	3.2
0.6372	0.1122	0.2506	0.948319	−9.40425	−5.36428	913.472	−106.344	3.1
0.5203	0.4027	0.0777	0.968157	−9.14121	−9.25434	1826.42	−162.521	3.3
0.5323	0.3078	0.1599	0.959177	−9.16710	−12.3864	2420.02	−202.516	3.0
0.5410	0.2143	0.2447	0.950406	−9.29451	−11.5505	1714.55	−127.781	3.2
0.5608	0.1112	0.3280	0.942108	−9.34130	−8.39770	414.888	−34.9482	3.4
0.4139	0.5099	0.0762	0.969972	−9.15035	−1.84616	−599.660	39.6324	3.1
0.4244	0.4142	0.1614	0.960671	−9.28004	−4.15890	556.721	−70.9668	3.2
0.4348	0.3232	0.2420	0.952413	−9.41046	0.75946	−1032.00	40.9524	2.9
0.4488	0.2119	0.3321	0.943184	−9.38323	−12.4208	1991.82	−168.015	2.7
0.4614	0.1118	0.4268	0.933859	−9.56620	−7.09090	632.104	−63.5197	2.9
0.3116	0.6106	0.0778	0.971079	−8.91552	−16.3407	3072.96	−259.634	2.7
0.3199	0.5216	0.1558	0.962535	−9.12491	−8.40210	620.217	−47.7658	2.6
0.3276	0.4271	0.2453	0.953775	−9.39151	−1.51628	−644.370	30.2931	3.0
0.3363	0.3311	0.3326	0.944732	−9.56374	−6.91940	1446.02	−153.056	2.1
0.3476	0.2230	0.4294	0.934856	−9.48772	−6.37590	−84.0632	5.11900	2.6
0.3921	0.1286	0.4793	0.929854	−9.64159	−8.14508	863.122	−80.9459	2.4
0.2088	0.7129	0.0783	0.972302	−8.90484	−22.9521	4929.89	−388.231	2.5
0.2128	0.6253	0.1619	0.963299	−9.10180	−7.75601	436.341	−39.6414	2.6
0.2187	0.5380	0.2433	0.954808	−9.33125	−4.77818	−18.0792	−16.6947	2.6
0.2264	0.4391	0.3345	0.945508	−9.59180	1.71003	−1069.17	41.5870	2.5
0.2349	0.3395	0.4256	0.936176	−9.51032	−6.01538	951.362	−169.262	2.7
0.2413	0.2311	0.5276	0.927249	−9.91904	−2.72407	70.3663	−41.2908	2.7
0.2458	0.1188	0.6354	0.918071	−10.2766	−1.36820	631.319	−107.082	2.5
0.1057	0.8158	0.0785	0.972794	−9.08452	7.34339	−2367.65	107.964	2.7
0.1076	0.7303	0.1621	0.964092	−9.21177	1.82492	−1745.28	123.319	2.4
0.1104	0.6452	0.2444	0.955528	−9.43119	−1.47689	−137.279	−23.8156	2.4
0.1120	0.5559	0.3321	0.942180	−9.63566	−2.74061	258.668	−76.1484	2.5
0.1172	0.4523	0.4305	0.937152	−9.31422	−16.1158	1471.86	−99.0246	2.3
0.1183	0.3502	0.5315	0.927310	−9.75055	4.54766	−3338.93	263.004	2.1
0.1238	0.2394	0.6368	0.917625	−9.74397	−6.67118	−512.007	34.3144	2.1
0.1283	0.1242	0.7475	0.908275	−9.86352	−9.09791	3.12108	15.2021	2.1

Table 3. b_{jk} Coefficients of Eq. 4 for DMF(1)/ME(2)/DME(3) Ternary Mixtures at Various Temperatures

Variable quantity	−10 °C	−5 °C	0 °C	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C
	0.897842	0.892777	0.887677	0.882538	0.877355	0.872123	0.866838	0.861498	0.856099	0.850642
X_2	8.68402×10^{-2}	8.53606×10^{-2}	8.31336×10^{-2}	8.02962×10^{-2}	7.69590×10^{-2}	7.32525×10^{-2}	6.92913×10^{-2}	6.51652×10^{-2}	6.09927×10^{-2}	5.68218×10^{-2}
X_2^2	-1.54637×10^{-2}	-3.37862×10^{-3}	9.22214×10^{-3}	2.23852×10^{-2}	3.62654×10^{-2}	5.08266×10^{-2}	6.60250×10^{-2}	8.18651×10^{-2}	9.81063×10^{-2}	1.14767×10^{-1}
X_2^3	6.76432×10^{-2}	4.53792×10^{-2}	2.49456×10^{-2}	5.65799×10^{-3}	-1.33243×10^{-2}	-3.24667×10^{-2}	-5.21341×10^{-2}	-7.27293×10^{-2}	-9.41612×10^{-2}	-1.16688×10^{-1}
X_2^4	-4.65265×10^{-2}	-3.36976×10^{-2}	-2.26221×10^{-2}	-1.27644×10^{-2}	-3.51241×10^{-3}	5.53502×10^{-3}	1.46974×10^{-2}	2.43072×10^{-2}	3.44108×10^{-2}	4.52146×10^{-2}
X_1	6.94666×10^{-2}	7.13914×10^{-2}	7.27810×10^{-2}	7.38268×10^{-2}	7.47346×10^{-2}	7.56300×10^{-2}	7.66384×10^{-2}	7.78162×10^{-2}	7.92094×10^{-2}	8.08208×10^{-2}
X_1X_2	2.19303×10^{-1}	1.89845×10^{-1}	1.87558×10^{-1}	2.06331×10^{-1}	2.40880×10^{-1}	2.87119×10^{-1}	3.40981×10^{-1}	3.99369×10^{-1}	4.59626×10^{-1}	5.20113×10^{-1}
$X_1X_2^2$	−1.44559	−1.23532	−1.14068	−1.13803	−1.20751	−1.33449	−1.50272	−1.69992	1.91502	2.14090
$X_1X_2^3$	1.84901	1.40838	1.16507	1.08132	1.12555	1.27542	1.50369	1.79130	2.11934	2.47548
$X_1X_2^4$	-6.08908×10^{-1}	-3.54626×10^{-1}	-2.04231×10^{-1}	-1.38793×10^{-1}	-1.42308×10^{-1}	-2.04171×10^{-1}	-3.09921×10^{-1}	-4.50394×10^{-2}	6.15655×10^{-1}	-7.99044×10^{-1}
X_1^2	5.83241×10^{-2}	4.74659×10^{-2}	4.04521×10^{-2}	-3.61550×10^{-2}	3.34277×10^{-2}	3.15226×10^{-2}	2.97208×10^{-2}	2.76179×10^{-2}	2.48924×10^{-2}	2.14209×10^{-2}
$X_1^2X_2$	−1.08650	-8.46184×10^{-1}	-7.63885×10^{-1}	-8.01193×10^{-1}	-9.25209×10^{-1}	−1.11069	−1.33333	−1.57410	−1.81787	−2.05508
$X_1^2X_2^2$	6.95853	5.25990	4.35573	4.06460	4.23104	4.73818	5.46690	6.32592	7.23964	8.15858
$X_1^2X_2^3$	−5.49295	−2.18294	-3.00030×10^{-1}	4.69729×10^{-1}	4.02342×10^{-1}	-3.01446×10^{-1}	−1.42416	−2.81381	−4.33173	−5.88879
$X_1^2X_2^4$	-1.96132×10^{-1}	−1.79370	−2.71700	−3.11068	−3.10813	−2.79704	−2.28540	−1.63861	-9.22351×10^{-1}	-1.78925×10^{-1}
X_1^3	-1.18498×10^{-1}	-9.76642×10^{-2}	-8.33837×10^{-2}	-7.38418×10^{-2}	-6.72407×10^{-2}	-6.23844×10^{-2}	-5.81354×10^{-2}	-5.38099×10^{-2}	-4.88654×10^{-2}	-4.30566×10^{-2}
$X_1^3X_2$	1.49099	1.03778	8.60281×10^{-1}	8.90049×10^{-1}	1.06863	1.35059	1.69325	2.06294	2.43322	2.78716
$X_1^3X_2^2$	−8.63501	−5.24882	−3.35336	−2.60342	−2.69357	−3.39182	−4.47065	−5.75810	−7.11233	−8.43888
$X_1^3X_2^3$	−2.30350	−8.37021	−11.8861	−13.4147	−13.4906	−12.4912	−10.8214	−8.74673	−6.51549	−4.28933
$X_1^3X_2^4$	6.46769	8.44771	9.64048	10.2068	10.3349	10.1144	9.69270	9.13091	8.50090	7.85500
X_1^4	7.20108×10^{-2}	6.03177×10^{-2}	5.19083×10^{-2}	4.59065×10^{-2}	4.14603×10^{-2}	3.80001×10^{-2}	3.49846×10^{-2}	3.20816×10^{-2}	2.90261×10^{-2}	2.56920×10^{-2}
$X_1^4X_2$	-5.67727×10^{-1}	-3.24208×10^{-1}	-2.25405×10^{-1}	-2.34999×10^{-1}	-3.22066×10^{-1}	-4.62334×10^{-1}	-6.33266×10^{-1}	-8.17260×10^{-1}	−1.00037	−1.17361
$X_1^4X_2^2$	3.10077	1.25278	1.73433×10^{-1}	-3.15180×10^{-1}	-3.75178×10^{-1}	-1.27470×10^{-1}	3.07945×10^{-1}	8.45839×10^{-1}	1.41356	1.96243
$X_1^4X_2^3$	6.26731	8.64566	10.0697	10.7467	10.8971	10.6480	10.1695	9.54098	8.85357	8.16572
$X_1^4X_2^4$	−2.12025	−1.33611	-9.65627×10^{-1}	9.09953×10^{-1}	−1.11514	−1.47348	−1.95804	−2.49062	−3.01913	−3.51706
$\sigma(\rho)$	7.3×10^{-4}	7.2×10^{-4}	7.2×10^{-4}	7.3×10^{-4}	7.3×10^{-4}	7.4×10^{-4}	7.5×10^{-4}	7.6×10^{-2}	7.7×10^{-4}	7.8×10^{-4}

Table 3. (Continued)

Variable quantity	40 °C	45 °C	50 °C	55 °C	60 °C	65 °C	70 °C	75 °C	80 °C
	0.845126	0.839552	0.833919	0.828233	0.822494	0.816707	0.810877	0.805009	0.799110
X_2	5.27380×10^{-2}	4.87946×10^{-2}	4.50554×10^{-2}	4.15399×10^{-2}	3.82992×10^{-2}	3.53553×10^{-2}	3.26863×10^{-2}	3.03353×10^{-2}	2.82692×10^{-2}
X_2^2	1.31599×10^{-1}	1.48440×10^{-1}	1.65003×10^{-1}	1.81072×10^{-1}	1.96279×10^{-1}	2.10241×10^{-1}	2.22732×10^{-1}	2.33145×10^{-1}	2.41103×10^{-1}
X_2^3	-1.40071×10^{-1}	-1.64149×10^{-1}	-1.88494×10^{-1}	-2.12693×10^{-1}	-2.36058×10^{-1}	-2.57780×10^{-1}	-2.77229×10^{-1}	-2.93125×10^{-1}	-3.04437×10^{-1}
X_2^4	5.66485×10^{-2}	6.86676×10^{-2}	8.10656×10^{-2}	9.36213×10^{-2}	1.05956×10^{-1}	1.17608×10^{-1}	1.28178×10^{-1}	1.36926×10^{-1}	1.43206×10^{-1}
X_1	8.25992×10^{-2}	8.44706×10^{-2}	8.63431×10^{-2}	8.80514×10^{-2}	8.94232×10^{-2}	9.02205×10^{-2}	9.01896×10^{-2}	8.90639×10^{-2}	8.64710×10^{-2}
X_1X_2	5.79779×10^{-1}	6.37895×10^{-1}	6.94672×10^{-1}	7.51159×10^{-1}	8.08633×10^{-1}	8.69395×10^{-1}	9.36428×10^{-1}	1.01274	1.10298
$X_1X_2^2$	−2.37244	−2.60424	−2.83608	−3.06926	−3.30588	−3.55229	−3.81614	−4.10579	−4.43486
$X_1X_2^3$	2.85110	3.23499	3.62609	4.02369	4.42922	4.85063	5.29656	5.77820	6.31359
$X_1X_2^4$	-9.96284×10^{-1}	−1.20075	−1.41166	−1.62771	−1.84901	−2.07884	−2.32023	−2.57819	−2.86055
X_1^2	1.73947×10^{-2}	1.30903×10^{-2}	8.91068×10^{-3}	5.56800×10^{-3}	3.94843×10^{-3}	5.11430×10^{-3}	1.03043×10^{-2}	2.08331×10^{-2}	3.85029×10^{-2}
$X_1^2X_2$	−2.28097	−2.49247	−2.69248	−2.88910	−3.09314	−3.32134	−3.59339	−3.93264	−4.37034
$X_1^2X_2^2$	9.05780	9.91110	10.7290	11.5385	12.3814	13.3284	14.4557	15.8669	17.6920
$X_1^2X_2^3$	−7.44721	−8.95182	−10.4227	−11.8994	−13.4579	−15.2175	−17.3042	−19.9031	−23.2348
$X_1^2X_2^4$	5.80503×10^{-1}	1.32755	2.07409	2.83863	3.66212	4.60176	5.71543	7.09744	8.85168
X_1^3	-3.66342×10^{-2}	-2.99663×10^{-2}	-2.36181×10^{-2}	-1.86096×10^{-2}	-1.63009×10^{-2}	-1.82050×10^{-2}	-2.61961×10^{-2}	-4.22336×10^{-2}	-6.90292×10^{-2}
$X_1^3X_2$	3.11762	3.41959	3.69875	3.97032	4.25521	4.58434	4.99296	5.52539	6.23848
$X_1^3X_2^2$	−9.70517	−10.8676	−11.9550	−13.0312	−14.1983	−15.6069	−17.4174	−19.8596	−23.2044
$X_1^3X_2^3$	−2.09427	-1.74792×10^{-2}	2.00036	4.06514	6.37556	9.18554	12.7692	17.5428	23.9685
$X_1^3X_2^4$	7.16744	6.46875	5.72842	4.90073	3.89262	2.61240	9.68250×10^{-1}	−1.21436	−4.08952
X_1^4	2.21913×10^{-2}	1.86902×10^{-2}	1.54393×10^{-2}	1.29101×10^{-2}	1.17482×10^{-2}	1.26349×10^{-2}	1.64577×10^{-2}	2.41219×10^{-2}	3.69034×10^{-2}
$X_1^4X_2$	−1.33386	−1.47851	−1.61076	−1.73902	−1.87499	−2.03543	−2.23924	−2.51083	−2.88082
$X_1^4X_2^2$	2.48478	2.95978	3.40683	3.86561	4.39953	5.09319	6.03802	7.36716	9.23029
$X_1^4X_2^3$	7.45144	6.74176	5.99781	5.15631	4.10593	2.72992	8.98734×10^{-1}	−1.59489	−4.94969
$X_1^4X_2^4$	−3.92237	−4.22001	−4.39479	−4.42881	−4.29964	−4.01607	−3.59596	−3.02029	−2.34277
$\sigma(\rho)$	7.8×10^{-4}	7.8×10^{-4}	7.9×10^{-4}	7.9×10^{-4}	8.1×10^{-4}	8.4×10^{-4}	8.9×10^{-4}	9.7×10^{-4}	10×10^{-4}

Excess Molar Volume (V^E). Generally, excess properties are considered indexes of the shift of real systems from ideality. According to literature suggestions regarding binary mixtures,[12] and extending the investigation to multicomponent solvent systems, the excess molar volume (V^E) may be evaluated starting from density measurements by means of the equation

$$V^E = \sum_{i=1}^{3} X_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right), \quad (5)$$

where M_i are the molar masses ($M_1 = 73.090$, $M_2 = 76.096$, $M_3 = 90.124$ g mol^{-1}) of the pure components, ρ and ρ_i refer to the densities of the mixtures and of the pure species at each temperature, respectively.

The calculations performed with Eq. 5 provide V^E values which are generally negative at all the experimental conditions, with some exceptions at the highest temperatures and in perfect agreement with the findings about the binary mixtures. Firstly, we should briefly examine the behavior of the three binary subsystems. The trend of V^E vs. X_{ME} for DMF/ME mixtures shows a pronounced minimum which becomes deeper as the temperature increases from −10 up to +80 °C. However, this minimum shifts at different composition ratios being centred at DMF : ME = 1 : 2 at −10 °C to 1 : 1 at 80 °C.

In the case of the DMF/DME binary solvent system, the V^E vs. X_{DME} plots always show negative deviations, with a sharp minimum in this property always centered at $X_{DME} \simeq 0.5$ at all experimental conditions.

Finally, as far as the ME/DME binary mixtures are concerned, one can note that V^E is negative at low temperatures (from −10 up to 15 °C), while positive and negative values are detected at temperatures higher than 15 °C. This picture seems to be quite intriguing, being observed for this binary solvent system two separate maxima in the pure rich-regions and is attributed to probable interstitial solvation phenomena, while a clear minimum is always present at each temperature and near to 1 : 1 stoichiometric ratio. For more details about these questions, the readers should refer to our previous published papers.[6,8,9]

For comparison purposes, Fig. 1 shows the plot of V^E against binary composition of DMF/ME, ME/DME, and DMF/DME at 25 °C. The solid curves have been obtained by fitting the isothermal V^E quantities to an equation of the type[13]

$$V^E = X_1 X_2 \sum_{0}^{k} c_k (X_2 - X_1)^k, \quad (6)$$

which allows us to recalculate the initial values, for a suitable k degree, in the limits of the experimental error at each composition.

In the present case, the V^E vs. X_i curves exhibit a minimum which becomes deeper in the sequence DMF/ME < ME/DME < DMF/DME, and the ME/DME binary system only shows a very slight positive deviation. This deviation, located in the DME rich region, probably could be attributed to interstitial solvation phenomena involving the complex moieties ME·DME and a certain number of molecules of the component which is in excess (DME). Probably, this phenomenology could also be well described in terms of "cage model" or "iceberg structures formation"[14] on the basis of which local density fluctuations can be related to long-range specific interactions between molecules associated to form primary clusters.

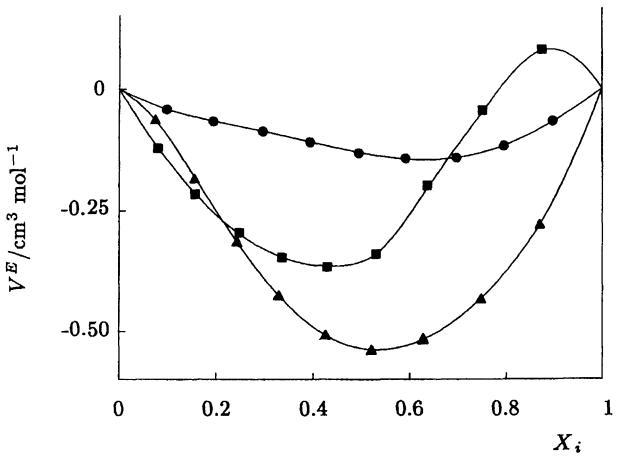

Fig. 1. Excess molar volumes (V^E/cm^3 mol^{-1}) against X_2 for the three binary subsystems at 25 °C: (●) DMF(1)/ME(2); (■) ME(1)/DME(2); (▲) DMF(1)/DME(2).

As the temperature increases up to *circa* 50 °C, a second positive maximum is observed in the trend of V^E vs. X_2 for these binary mixtures, located in proximity of the ME rich-region, and beyond this temperature the expansion ($V^E > 0$) is enhanced.[8]

Returning now to the trend of Fig. 1 on the whole, the minimum seems to be centered at $X_i \simeq 0.65$ for DMF/ME, and at $X_i \simeq 0.5$ for the other binary mixtures. Furthermore, the two DMF containing binary systems show that V^E tends to decrease by increasing the temperature, while the contrary is observed for the ME/DME mixtures. These evidences can be partly accounted for by the assumption that deviations of V^E from ideal behavior are a consequence of specific interactions (such as hydrogen bonding, dipole–dipole, dipole–induced dipole) which take place between unlike species.[2] However, it should be useful to mention that another very important factor occurring in modulating the V^E quantity is of geometrical nature, being related to the molecular shape of pure species. In this light it is possible to try to rationalize the trend of Fig. 1, in particular for the DMF containing mixtures. In fact, it is well known that both ME and DME can exist in the two rotameric *anti* and *gauche* conformers, being the *gauche* rotamer preferred by ME (with a relatively strong intramolecular hydrogen bond)[15] and the *anti* by DME[16] molecules. The shift from ideal-

ity, greater for the DMF/DME than for the DMF/ME system, probably should arise from the reciprocal accomodation of DMF and DME molecules, better than in the case of DMF and ME.

According to other authors,[17] the study of the excess thermophysical properties of binary mixed liquids could be very useful, in addition to IR and NMR techniques, in order to investigate the formation of solvent–cosolvent adducts, and could provide valuable help to determine their stoichiometry (in correspondence of maxima deviations from ideality) as well as their thermostability. Following the above considerations, we can suggest the composition ration 1DMF·2ME, 1DMF·1DME, and 1ME·1DME for the stable complex moieties in the corresponding binary systems at 25 °C.

For ternary mixtures, the literature is quite poor in providing reliable equations to fit the excess thermochemical properties; therefore the relationship

$$V^{E}=d_1X_1X_2+d_2X_2X_3+d_3X_1X_3 +d_4X_1X_2(X_2-X_1)+d_5X_2X_3(X_3-X_2) +d_6X_1X_3(X_3-X_1)+d_7X_1X_2X_3 \quad (7)$$

has been applied to our isothermal V^{E} quantities, in an attempt to obtain the best representation of the excess property. An equation like (7) has been previously used by Katz et al. in a previous work.[18]

It should be noted that Eq. 7, formally deriving from the Redlich–Kister one[13] with $k=1$, simulates the V^{E} values for a ternary solvent system mainly as a sum of contributions due to the three binary subsystems, being the overall ternary mixture effect explicitly contained into the d_7 term only. The fitting coefficients of Eq. 7 are given in Table 4, together with the standard error of determination $\sigma(V^{E})$ at each investigated temperature. Equation 7 recalculates the V^{E} values with an average uncertainty $\overline{\Delta V^{E}}=\pm 0.046$ cm^3 mol^{-1} over all the 1254 input data, considering the ternary system on the whole.

To test the presence of three-component adducts in these liquid mixtures, we have plotted the V^{E} quantity at each selected temperature in the ternary composition domain $\{X_1,X_2,X_3\}$ and the results, at −10, 25, and 80 °C for example, are displayed in the Figs. 2 and 3. A careful examination of these plots provides no evidence of stable three component adducts in this ternary solvent system, being absent in the graphs relative minima other than those of the binary subsystems.

However, by examining these figures, one can note that a series of singular points in the ternary domain $\{X_1,X_2,X_3\}$ are present, corresponding to $V^{E}=0$, at each selected temperature $t\geq 25$ °C. Obviously, for $V^{E}=0$ the ternary mixtures show "ideal volumic" behavior, even though the three components are polar and therefore strongly interacting one another. In this respect, we notice that this "ideal" behavior can probably result from a compensation of different effects, being observed that V^{E} assumes different signs ($V^{E}<0$ and $V^{E}>0$) in the ternary domain, rather than being the result of the mixing process of ideal components.

We wish to thank Professor Carlo Preti for helpful suggestions and continuous interest on this research program. The Ministero dell'Università e della Ricerca Scientifica e Tecnologica (M.U.R.S.T.) of Italy is gratefully acknowledged for the financial support.

Table 4. Coefficients d_i of Eq. 7 for DMF(1)/ME(2)/DME(3) Ternary Mixtures at Various Temperatures

t/°C	d_1	d_2	d_3	d_4	d_5	d_6	d_7	$10^2\sigma(V^{E})$
−10	−0.4342	−1.7713	−1.4469	0.1959	0.8388	−1.2795	3.3072	8.1
−5	−0.4099	−1.6752	−1.5011	0.1613	0.6590	−1.1555	3.1454	8.1
0	−0.3996	−1.5684	−1.5758	0.1272	0.5573	−1.0520	2.9132	8.0
5	−0.4016	−1.4524	−1.6675	0.0923	0.5205	−0.9696	2.6112	7.9
10	−0.4131	−1.3284	−1.7728	0.0570	0.5321	−0.9074	2.2341	7.7
15	−0.4324	−1.1976	−1.8886	0.0209	0.5796	−0.8655	1.7834	7.6
20	−0.4579	−1.0613	−2.0122	−0.0158	0.6506	−0.8437	1.2615	7.5
25	−0.4873	−0.9205	−2.1404	−0.0534	0.7335	−0.8408	0.6696	7.5
30	−0.5194	−0.7761	−2.2712	−0.0920	0.8189	−0.8562	0.0132	7.5
35	−0.5526	−0.6284	−2.4019	−0.1313	0.8980	−0.8883	−0.7018	7.6
40	−0.5859	−0.4781	−2.5308	−0.1720	0.9644	−0.9353	−1.4672	7.9
45	−0.6179	−0.3250	−2.6558	−0.2129	1.0125	−0.9961	−2.2720	8.0
50	−0.6480	−0.1700	−2.7764	−0.2543	1.0382	−1.0683	−3.1048	8.4
55	−0.6753	−0.0112	−2.8898	−0.2957	1.0401	−1.1490	−3.9547	8.8
60	−0.6989	0.1506	−2.9966	−0.3365	1.0172	−1.2367	−4.8036	9.4
65	−0.7196	0.3169	−3.0955	−0.3774	0.9720	−1.3253	−5.6322	10
70	−0.7361	0.4897	−3.1857	−0.4167	0.9076	−1.4135	−6.4239	11
75	−0.7489	0.6697	−3.2686	−0.4538	0.8302	−1.4963	−7.1541	12
80	−0.7587	0.8602	−3.3430	−0.4897	0.7491	−1.5689	−7.7989	13

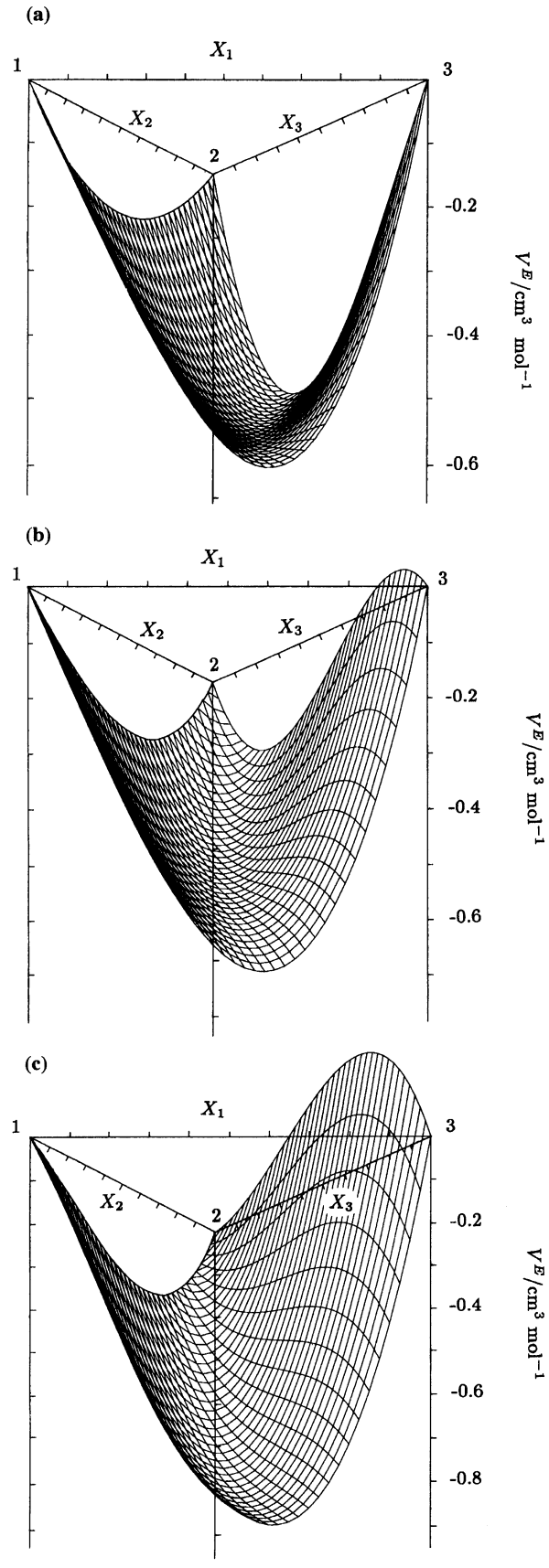

Fig. 2. Pictorial view of the V^E -composition X_i surface for DMF(1)+ME(2)+DME(3) ternary solvent system: a) −10 °C; b) 25 °C; c) 80 °C.

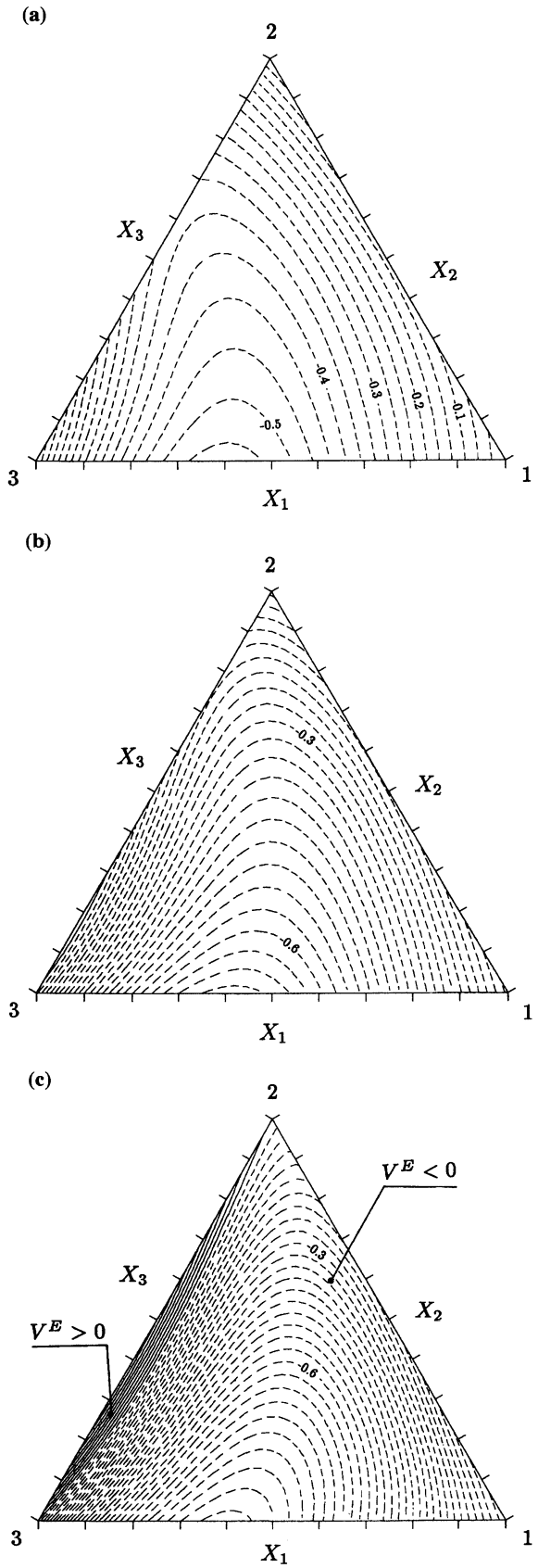

Fig. 3. Computer generated contour diagram showing lines of constant V^E on a liquid mole fraction grid DMF(1)+ME(2)+DME(3): a) −10 °C b) 25 °C; c) 80 °C.

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