Dielectric Characterization of Binary Solvents Containing 1,2-Dichloroethane and 2-Chloroethanol

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Static dielectric constants (ε) were determined for the 1,2-dichloroethane (DCE, 1)/2-chloroethanol (CE, 2) binary solvent system at 19 temperatures ranging from −10 to +80 °C and in the whole composition range expressed by the mole fraction $0 \le X_1 \le 1$. The experimental values have been fitted to some equations that could be usefully employed for predictive ε calculations. Furthermore, the excess mixing properties (ε^E) have been evaluated in order to point out the presence of solvent–cosolvent adducts in the binary mixtures mentioned above. The values of ε^E have been generally found to be negative and only slightly positive under a few experimental conditions in the CE rich-region, thus giving evidence of a close interaction network probably via hydrogen bonding as well as other interactions of every kind in this solvent system.

It is well-known that the thermophysical properties of liquid systems (such as density, viscosity, dielectric constant, refractive index, and related quantities) play a key role in electroanalytical processes in solution and are related to their optimization, which in turn is one of the main objectives of material science.[1] As a consequence, the development of forecasting methods for the estimation of thermophysical properties, which should be as accurate as possible and widely applicable, is a primary target of many studies concerning thermomechanic properties research in chemical engineering design and in applied chemistry, as far as theoretical studies are concerned.

In this connection and according to general opinion, no correlation for a given thermophysical property can be both accurate and widely applicable, unless it is based on an comprehensive understanding of the molecular processes which account for this property. The recognition of these facts has led many research workers in a concerted effort to elucidate the microscopic basis for thermomechanic properties of solutions, either electrolytic or not.[2]

Therefore, the macroscopic and measurable properties of these systems, which originate from the specific interactions and structural effects which occur in solution, represent an effective means, in addition to spectroscopic techniques, for the investigation of interactions at the molecular level and of their microscopic effects. Following these research lines, the subject of this paper will be a study of the dielectric properties of a mixed liquid system containing 1,2-dichloroethane (DCE, component 1)+2-chloroethanol (CE, component 2), at 19 temperatures ranging from −10 to +80 °C, employing the two pure species and 9 of their binary mixtures covering the whole miscibility field expressed by the relation $0 \le X_1 \le 1$.

Even though CE has proved to be an extremely interesting species for various theoretical applications in recent years,[3,4] it seems to us that this solvent has been only slightly reviewed as to its thermomechanical properties,[5] in spite of its strategic importance in many industrial applications, i.e. as an intermediate for epoxyresins production.

On the other hand, DCE has been largely utilized by many research workers for electroanalytical studies,[6,7] and its practical importance is stressed by its massive employment as a versatile and efficacious halogenated solvent for fats, oils, polymers science, and many other industries.

On the basis of these considerations, we decided to extend our research program on the thermophysical properties of multicomponent solvent systems to these species as well, enriching in this way our data bank based on 1,2-ethanediyl derivatives such as 1,2-ethanediol (ED),[8] 2-methoxyethanol (ME),[9] 1,2-dimethoxyethane (DME),[10] and 1,4-dioxane (DX).[11]

Experimental

Materials. The solvents 1,2-dichloroethane and 2-chloroethanol (both with water content less than 0.10% by mass, as determined by Karl–Fischer titrations) were high purity grade reagents produced by Carlo Erba (Milan). Both solvents were further purified by simple distillation over $NaKCO_3$ anhydrous to eliminate traces of acids and to reduce the water content, keeping the middle fraction only (bp 83.5 °C for DCE, and 128.5 °C for CE) for the measurements. Both solvents were preserved on 3 Å molecular sieves for many days before use, and the final purity was checked by gas chromatography (99.8 % DCE, 99.7 % CE, by mass), confirming the absence of significant amounts of other organic components.

Apparatus and Procedures. The mixtures were prepared just before use by weighing them on a Mettler PM 4800 Δ-range balance, operating in a dry box in order to avoid atmospheric moisture, and then preserved on 3 Å molecular sieves. The probable error in each mole fraction (X_i) is estimated to be less than 1.5×10^{-4}.

The equipment and the experimental procedures for standardization of cells and static dielectric constant measurements have been described elsewhere.[12)]

The experiments were generally repeated at least 10 times for each composition and at each temperature, with a confidence interval of 95%, and the results were averaged. The reproducibility of the measurements, expressed as the standard deviation $\sigma(\varepsilon)$, was approximately ±0.2% and the estimated accuracy was $\pm1.2\times10^{-4}$.

Results and Discussion

Dielectric constants were measured as a function of temperature for pure solvents as well as for nine mixtures. The experimental values are summarized in Table 1 together with the binary composition expressed in different scales. Our ε values for pure species have been compared with the literature values reported by Maryott and Smith, and we notice that low agreement is present (ε=10.36 for DCE and 25.8 for CE at 25 °C, respectively).[13)] Unfortunately, the values' comparison is very limited and therefore any speculation about it will be avoided.

The experimental ε values are related to the absolute temperature (T/K) by means of the equation[14)]

$$\ln \varepsilon = \sum_{i=0}^{1} \alpha_i T^i, \tag{1}$$

where α_i are adjustment parameters, evaluated by a fitting procedure[15)] and are summarized in Table 2, together with the standard deviation $\sigma(\ln \varepsilon)$ for each binary mixture. Equation 1 reproduces the experimental data within an average uncertainty $\overline{\Delta\varepsilon}=\pm0.02$ ($0.00\leq|\Delta\varepsilon|\leq0.05$) evaluated as follows

$$\overline{\Delta\varepsilon} = \frac{1}{N}\sum_{N}|\varepsilon_{\text{calcd}} - \varepsilon_{\text{exptl}}|, \tag{2}$$

where N (209) are the values of Table 1.

A further step of this study was an investigation of the dependence of ε on the binary composition of liquid mixtures. For this purpose, the experimental ε values have been isothermally plotted as a function of X_2

Table 2. Coefficients α_i and Standard Deviations σ ($\ln \varepsilon$) of Eq. 1 for DCE(1)+CE(2) Binary Mixtures

System	α_0	$10^3\alpha_1$	$10^3\sigma$ ($\ln \epsilon$)
A	3.78850	−4.75283	2.3
B	3.88676	−4.84797	1.8
C	4.01833	−4.98961	1.7
D	4.18235	−5.21132	1.6
E	4.36496	−5.45770	1.4
F	4.50756	−5.63843	1.4
G	4.67036	−5.85622	1.2
H	4.78913	−5.96576	0.7
I	4.92371	−6.16338	0.8
L	5.04725	−6.29867	0.7
M	5.21550	−6.68954	0.8

Table 1. Experimental Static Dielectric Constants for the DCE(1)+CE(2) Binary Mixtures at Various Temperatures

X_1	1.0000	0.8893	0.7792	0.6722	0.5562	0.4634	0.3603	0.2693	0.1825	0.0853	0.0000
V_1/V_2 (%)[a)]	100/0	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90	0/100
T/K	A	B	C	D	E	F	G	H	I	L	M
263.15	12.70	13.65	15.01	16.66	18.74	20.61	22.91	25.02	27.21	29.63	31.68
268.15	12.39	13.27	14.58	16.22	18.21	20.02	22.19	24.27	26.33	28.72	30.63
273.15	12.09	12.99	14.26	15.81	17.73	19.46	21.58	23.57	25.54	27.84	29.62
278.15	11.79	12.65	13.89	15.36	17.24	18.90	20.93	22.86	24.77	26.97	28.65
283.15	11.50	12.35	13.53	14.97	16.76	18.36	20.31	22.20	24.00	26.14	27.67
288.15	11.22	12.08	13.19	14.58	16.32	17.86	19.74	21.53	23.27	25.36	26.79
293.15	10.95	11.74	12.85	14.20	15.85	17.34	19.15	20.91	22.55	24.58	25.88
298.15	10.69	11.48	12.58	13.87	15.46	16.90	18.63	20.32	21.90	23.81	25.07
303.15	10.44	11.19	12.23	13.47	15.01	16.39	18.11	19.69	21.20	23.07	24.20
308.15	10.20	10.97	11.94	13.14	14.62	15.95	17.55	19.13	20.57	22.33	23.44
313.15	9.96	10.67	11.64	12.79	14.21	15.48	17.03	18.55	19.93	21.66	22.64
318.15	9.72	10.42	11.35	12.47	13.84	15.10	16.56	18.01	19.36	20.97	21.93
323.15	9.49	10.16	11.07	12.14	13.46	14.63	16.06	17.47	18.77	20.32	21.18
328.15	9.27	9.92	10.83	11.87	13.13	14.25	15.61	16.99	18.19	19.70	20.51
333.15	9.06	9.69	10.56	11.54	12.77	13.85	15.16	16.47	17.66	19.09	19.84
338.15	8.86	9.45	10.27	11.27	12.44	13.49	14.74	15.98	17.12	18.51	19.19
343.15	8.67	9.26	10.06	10.98	12.11	13.12	14.33	15.53	16.60	17.91	18.56
348.15	8.47	9.04	9.81	10.70	11.79	12.76	13.92	15.08	16.08	17.36	17.92
353.15	8.28	8.80	9.55	10.39	11.43	12.39	13.49	14.60	15.59	16.81	17.33

a) At 20 °C.

(Fig. 1). The trend shows a marked curvature at all temperatures studied. In order to represent this trend in analytical form, we applied to each isothermal set of experimental data a polynomial expansion of the type

$$\ln \varepsilon = \sum_{0}^{j} \beta_j X_1^j, \tag{3}$$

whose β_j fitting parameters (for $j=4$) are listed in Table 3 together with the standard deviation $\sigma(\ln \varepsilon)$ at each temperature. The effectiveness of this equation for predictive calculations in the presence of experimental data gaps is guaranteed on the basis of an average uncertainty $\overline{\Delta\varepsilon}=\pm 0.03$ referring to all 209 (N) values of Table 1, and ranging within $0.00 \leq |\Delta\varepsilon| \leq 0.05$.

In order to quicken the interpolation procedures, we also checked a single bivariant function of the type $\varepsilon=\varepsilon(T,X_1)$, which has been successfully applied in our previous studies.[8,9] This function is obtained by starting from Eqs. 1 and 3, and by simple algebraic manipulation of them:

$$\ln \varepsilon(T,X_1) = \sum_{0}^{i} \sum_{0}^{j} \gamma_{ij} T^i X_1^j. \tag{4}$$

This fitting relationship takes the γ_{ij} coefficients of Table 4, and reproduces the experimental ε data within $\overline{\Delta\varepsilon}=\pm 0.04$, with $|\Delta\varepsilon|$ values ranging from 0.00 to 0.15.

Excess Function. Deviations from ideal dielectric behavior for this binary system have been calculated based on the assumption of a linear dependence of the ε values on the mole fraction composition by applying an equation which formally derives from Raoult's law for ideal solutions.[16] The relation

$$\varepsilon^{\mathrm{E}} = \varepsilon - (\varepsilon_1 X_1 + \varepsilon_2 X_2), \tag{5}$$

where ε^{E} is the excess mixing property, and ε_1, ε_2

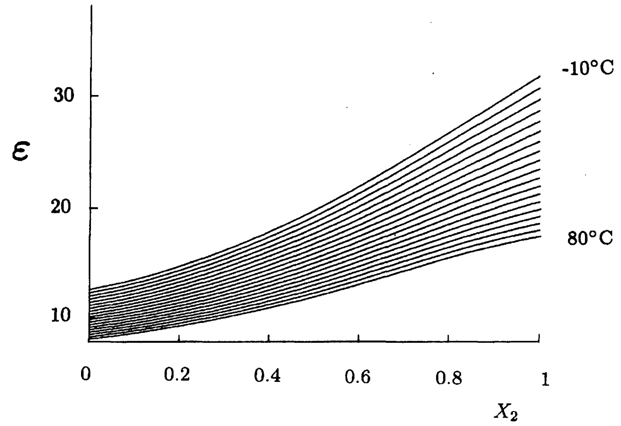


Fig. 1. Trend of ε against X_2 for DCE(1)/CE(2) solvent system.

Table 4. Coefficients γ_{ij} and Standard Deviation[a)] σ $(\ln \varepsilon)$ of the model equation $\varepsilon=\varepsilon(T,X_1)$ for DCE(1)+CE(2) Mixtures

ij	Variable quantity	γ_{ij}
00		5.20950
01	X_1	−1.88528
02	X_1^2	2.09623
03	X_1^3	−3.74818
04	X_1^4	2.11898
10	T	-6.66188×10^{-3}
11	TX_1	4.20724×10^{-3}
12	TX_1^2	-9.42377×10^{-3}
13	TX_1^3	1.42278×10^{-2}
14	TX_1^4	-7.11534×10^{-3}

a) σ $(\ln \varepsilon)=2.9\times10^{-3}$.

Table 3. Coefficients β_j and Standard Deviations σ $(\ln \varepsilon)$ of Eq. 3 for the DCE(1)+CE(2) Mixtures at Various Temperatures

T/K	β_0	$10\beta_1$	$10\beta_2$	$10^3\beta_3$	$10^4\beta_4$	$10^3\sigma$ $(\ln \epsilon)$
263.15	3.45642	−7.78152	−3.83520	−4.49405	2468.63	1.7
268.15	3.42313	−7.57434	−4.29131	64.2844	2124.53	1.8
273.15	3.38979	−7.35916	−4.78455	139.133	1748.58	2.0
278.15	3.35649	−7.15096	−5.24679	208.682	1401.99	2.2
283.15	3.32318	−6.93986	−5.72072	280.395	1042.25	2.3
288.15	3.28988	−6.72935	−6.19517	352.164	683.302	2.5
293.15	3.25658	−6.52001	−6.66011	422.165	333.462	2.7
298.15	3.22328	−6.31440	−7.10748	489.385	−1.73403	2.8
303.15	3.18993	−6.09656	−7.61558	566.752	−390.386	3.0
308.15	3.15662	−5.88446	−8.09162	638.135	−744.813	3.2
313.15	3.12335	−5.68179	−8.52985	704.542	−1078.88	3.4
318.15	3.09000	−5.46209	−9.04199	781.741	−1464.00	3.6
323.15	3.05670	−5.25627	−9.49420	849.957	−1804.41	3.8
328.15	3.02341	−5.04597	−9.97002	922.357	−2168.90	3.9
333.15	2.99009	−4.83092	−10.4608	996.080	−2535.05	4.1
338.15	2.95679	−4.62925	−10.8850	1059.53	−2852.43	4.3
343.15	2.92346	−4.41271	−11.3874	1135.91	−3235.38	4.5
348.15	2.89016	−4.20337	−11.8496	1204.75	−3576.19	4.7
353.15	2.85683	−3.99043	−12.3358	1278.75	−3947.40	4.8

are the dielectric constants of the pure components at each temperature, was first proposed by Payne and Theodorou[17)] for the calculation of dielectric constants of mixtures involving one or both highly polar components. Other theoretical relations, such as Clausius–Mosotti treatment, fail because of their limitations and failure to take into account the molecular dipole reaction field.[18)] In the present case, the two pure components are polar species, with dipole moments $\mu_{\mathrm{DCE}}=1.42$ D[19)] and $\mu_{\mathrm{CE}}=1.89$ D,[20)] (1 D$\approx 3.335\times10^{-12}$ C m).

The suitability of Eq. 5 has been tested in many cases and for a wide variety of mixed solvents, such as polar, apolar, protic, aprotic, amphiprotic, etc.[17)] The ε^{E} data have been plotted in Fig. 2 as a function of composition (X_2). These plots exhibit a broad minimum, slightly skewed toward the DCE-rich region, whose magnitude never exceeds −2.38 (mixture E at −10 °C) and that sharply decreases as the temperature increases. Furthermore, some positive ε^{E} values are present in the CE-rich region and at temperatures $t\geq30$°C, showing a slight maximum centered at $X_2\simeq0.9$. Dielectric constant excess data were fitted at each temperature to a smoothing equation of the following type:[21)]

$$\varepsilon^{\mathrm{E}} = X_1X_2\sum_{0}^{k} c_k(X_2-X_1)^k, \tag{6}$$

which allowed us to recalculate the excess dielectric constants within the limits of experimental error under all experimental conditions, being $\overline{\Delta\varepsilon^{\mathrm{E}}}=\pm0.02$, and always ranging between $0.00\leq|\Delta\varepsilon^{\mathrm{E}}|\leq0.08$. The fitting c_k coefficients (for k=0,1,2,3) of the smoothing equation, as well as the standard deviations $\sigma(\varepsilon^{\mathrm{E}})$ at each temperature, are summarized in Table 5.

A brief examination of the magnitude of the excess properties in this solvent system supplies evidence for the assumption that interaction energies of every kind are of moderate importance.[17)] However, the molecular dynamics of these species have been investigated by means of spectroscopic techniques,[22,23)] and a survey of this literature can provide a useful interpretive overview. It is well-recognized that both selected species can exist in the two limiting conformation structures, *anti* and *gauche*, as represented in the following Scheme 1. Now, while the DCE molecule seems to be more stable as the *anti* conformer (the relative amount of this rotamer as compared to *gauche*, showed a marked variation with temperature but always prevailed and ranged from 89.6% at −13 °C to 62.7% at 300 °C in the gas phase),[22)] the CE species is more preferably present as the *gauche* conformer.[23)] Spectroscopic analysis by electron diffraction at different temperatures in the range $37\leq t/°\mathrm{C}\leq200$, revealed that more of the trans rotamer is present at higher temperatures (≃20% trans) than at lower temperatures (less than 10% trans). The *gauche* conformer is stabilized by an intramolecu-

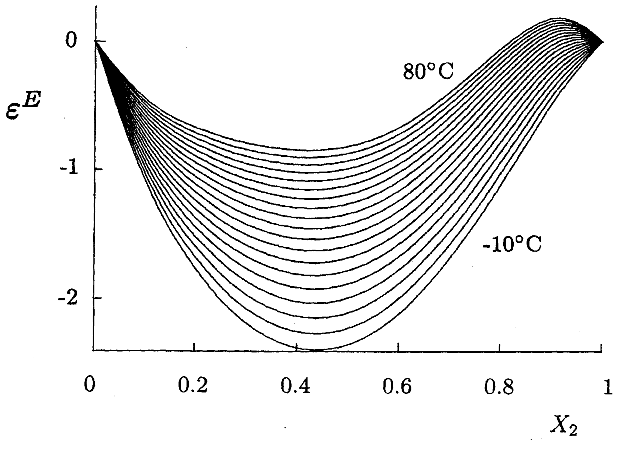
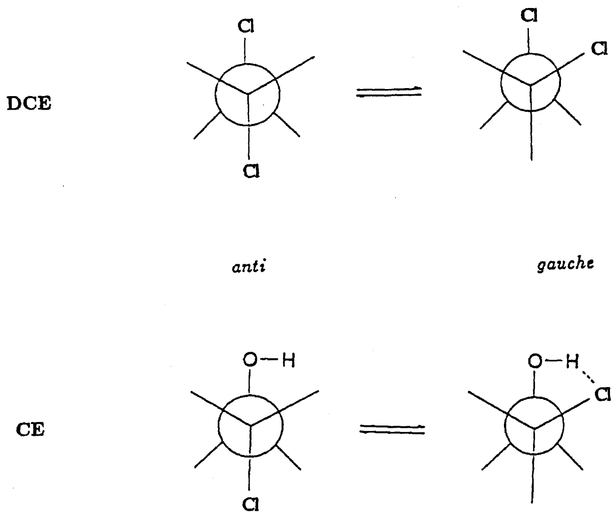


Fig. 2. Plots of ε^{E} against X_2 for DCE(1)/CE(2) solvent system.

Table 5. Coefficients c_i and Standard Deviations $\sigma(\varepsilon^{\mathrm{E}})$ of Eq. 6 for the DCE(1)+CE(2) Solvent System at Various Temperatures

T/K	c_0	c_1	c_2	c_3	$10^2\sigma$ (ε^{E})
263.15	−9.392	2.593	1.075	2.187	1.8
268.15	−8.899	2.539	1.239	2.388	2.0
273.15	−8.423	2.488	1.400	2.581	2.2
278.15	−7.975	2.430	1.549	2.779	2.4
283.15	−7.541	2.382	1.672	2.937	2.6
288.15	−7.131	2.322	1.801	3.112	2.9
293.15	−6.741	2.273	1.923	3.245	3.0
298.15	−6.366	2.223	2.014	3.370	3.2
303.15	−6.007	2.172	2.126	3.488	3.4
308.15	−5.668	2.121	2.217	3.599	3.6
313.15	−5.343	2.065	2.289	3.691	3.7
318.15	−5.032	2.021	2.377	3.777	3.9
323.15	−4.740	1.964	2.441	3.864	4.0
328.15	−4.459	1.914	2.507	3.935	4.1
333.15	−4.193	1.873	2.564	3.962	4.2
338.15	−3.935	1.820	2.598	4.032	4.3
343.15	−3.694	1.774	2.657	4.071	4.4
348.15	−3.464	1.722	2.692	4.132	4.4
353.15	−3.245	1.674	2.731	4.154	4.5



Scheme 1.

lar hydrogen bond whose energy is rougly estimated to be 15.9 kJ mol^{-1}.[23] Therefore, the conclusion may be drawn that differences in the properties of the pure components play the most important role in determining the intensity and shape of the excess function curves against a binary composition.

Still, as far as the trend in excess mixing properties with composition is concerned, it has been outlined in the literature that deviations from ideality in correspondence to relative minima or maxima in the plots could be related to the presence of stable solvent–cosolvent adducts in the binary mixtures,[24] and whose stoichiometric ratio can be fixed at the abscissa in correspondence to the largest deviations.

Therefore, in the present case we suggest that the more stable complex moiety should be DCE : CE=1 : 1, while the relative maximum at $X_2 \simeq 0.9$ (DCE : CE= 1 : 9) can be very likely attributed to interstitial solvation phenomena and microheterogenities, which should be responsible for an ordered supramolecular build-up and clusterization, rather than a solvent–cosolvent complex adduct involving such a high number of molecules.

As little is known about these mixtures, and in the absence of spectroscopic data, we may only hypothesize that the addition of DCE (up to about 10%) to CE is responsible for an increase in the ordered liquid structure, in agreement with the experimental observation that $\varepsilon^E > 0$ (mixture L at $t \geq 30$°C). Therefore, this picture should be coherent with an increase (even if small) of the *anti*-CE conformer population in order to maintain an effective hydrogen-bonding network around the complex adduct DCE·CE (interstitial solvation). In other words, the heteroaggregated moieties should be clusterized into a cavity (microheterogenieties), while solvating CE molecules should provide the ordered supramolecular build-up.

As previously pointed out, the presence of a flat minimum in ε^E against X_2 plots indicates that interactions of every kind between unlike molecules are present when they are coupled in more stable molecular pairs, and the resulting adducts can scarcely interact with one another. Furthermore, these specific interactions should be nearly of the same type as those observed in the CE pure species, being the same functional groups present in the component molecules and with intermolecular hydrogen bonding as the prevailing interaction pattern.

As a consequence, the intensity of these specific intermolecular interactions should not differ much from 15.9 kJ mol^{-1}, as observed in pure CE. A lessening of these interactions with increasing temperature accounts for the decrease of the minimum in the ε^E vs. X_2 curves.

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