

THE ETHYLENE CARBONATE-WATER SYSTEM: DENSITIES, VISCOSITIES AND DIELECTRIC CONSTANTS AT DIFFERENT TEMPERATURES

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(Received October 6, 1982; revised April 21, 1987)

The data obtained for density, viscosity and dielectric constant are used for the study of the physical properties of water-ethylene carbonate solvent mixtures. Density measurement of the solvent mixtures showed the presence of interaction between water and ethylene carbonate through hydrogen bonding which would lead to contraction in the volume of the mixture and also in the partial molal volume of the components. Viscosity data also provided supporting evidence of such interaction.

Key words: Solute-solvent interaction of binary system; Density-viscosity; dielectric constant measurements of binary mixture; Excess partial volume and deviation molar viscosity and dielectric constant for EC-H₂O system.

INTRODUCTION

Ethylene carbonate, CH₂CH₂CO₃ (EC) is a dipolar aprotic solvent with remarkable high dielectric constant ($D = 89.6$ at 40°). Furthermore it can be easily obtained in pure state. Although the freezing point of ethylene carbonate is 36.6°, this compound is miscible with water upto a composition of nearly 90 wt % of EC at 25° which permits the preparation of mixed solvents covering an extremely wide range of dielectric constants. The resultant Kirkwood value (g) for EC is some what higher, although still close to unity [1] ($g = 1.43$). Therefore, it is expected that some kind of association is present. Also, the absence of proton donor group in pure EC and the weaker basicity of the carbonyl group do not permit the association of the solvent by hydrogen bonding. According to the Kirkwood factor and the value of the association constant which was calculated by Bonner [2], a certain degree of association between the solvent molecules is observed.

From the above view the structural properties of the mixed system EC-water are of interest. Therefore density, viscosity, and dielectric constant measurements were expected to shed some more light on the structure of the solvent mixtures.

EXPERIMENTAL

Ethylene carbonate (BDH grade) was double distilled at reduced pressure and collected at 180°. The middle cut of the distillation was used for the density, viscosity, and dielectric constant measurements [3].

Density measurements for water-ethylene carbonate mixtures at 25, 30, 35, 40 and 45° were made by using a pycnometer of about 20 ml capacity. The pycnometer was calibrated with double distilled water at each temperature. A modified Ubelohde suspended level viscometer was used for viscosity measurements by comparing the flow of water-ethylene carbonate solvent mixtures with that of freshly prepared double distilled water whose viscosity is known at studied temperatures.

The apparatus used for the measurements of dielectric constant was a multi DeKameter type "DK06" which has a frequency range 0.1-12 MC/S. The adjustment was carried out on a cathode ray tube. The tuning condenser which has 4500 uniform divisions permitted fine adjustments and allowed a sensitivity of the order 10⁻⁵. It is important to point out that a frequency of 5 MC/S was used for the measurement of the scale reading (S) for pure water and water-ethylene carbonate mixtures.

The dielectric constant (D) of a solution was calculated using the equation:

$$D = AS + C \dots \dots \dots (1)$$

where S is the scale reading measured by the DeKameter. A and C are constants which can be readily evaluated by the least squares method taking into consideration pure water as a standard liquid. Substitution of the obtained values of the scale readings for pure water at different temperatures and the corresponding value of D (obtained from the literature) [4], the values A and C could be obtained and used for the evaluation of the dielectric

constants of ethylene carbonate-water mixtures at 30, 40 and 45°

RESULTS AND DISCUSSION

1. *Density.* Table 1 represents the calculated values of the absolute densities of ethylene carbonate-water mixtures at different temperatures. A comparison of the results with those obtained elsewhere [2] are also included.

The excess volume ΔV^E in this system was calculated from two different equations [5,6]. These are:

$$\frac{1}{d_{12}} = \frac{w_1}{d_1^0} + \frac{w_2}{d_2^0} + \delta \dots \dots \dots (2)$$

in which $\delta = \Delta V^E$

$$\text{and } \Delta V^E = \frac{X_1 M_1 + X_2 M_2}{d_{12}} - \left(X_1 \frac{M_1}{d_1^0} + X_2 \frac{M_2}{d_2^0} \right) \dots (3)$$

where, d_1^0 , d_2^0 and d_{12} are the densities of the pure components and solvent mixtures respectively, w_1 and w_2 are the mole fractions and the molecular weight of the two components respectively. ΔV^E from the two equations was calculated at 40 and 45°, since pure EC melts at 36.6°.

It can be easily seen from Fig. 1 that a distinctive minimum occurs at $X_1 \approx 0.17$ indicating solute-solvent interaction. This interaction can be interpreted knowing that water structure was looked upon [7] as flickering clusters of various sizes and shapes, jumping to attention, so to speak, and then relaxing "at ease" On the other hand, Cabon and Maurice [1] showed that ethylene carbonate molecules can be associated by the dipole-dipole interaction. The expected number for the associated molecules was 8. Accordingly on adding ethylene carbonate to water depolymerization occurs and interaction between EC and H₂O through hydrogen bond formation is permitted. This interpretation was also suggested by D'Aprano [8] for the same system.

According to the previous picture, the occurrence of the minimum at $X_1 \approx 0.17$ can be looked as an indication to cooperative effect among the organic molecules. This lies in the cooperative, specific participation of the solute molecules with water to form a clathrate type of structure [9]. Organic molecules help to form stabilize "holes" in the water structure. These holes are able to accommodate, at least partially, the solute molecules with a consequent economy of volume. On this basis the maximum structural

Table 1. Absolute density of ethylene carbonate-water mixtures at different temperatures.

EC %	Mole fraction of EC(X_1)	Absolute density				
		25°	30°	35°	40°	45°
0.0000	0.0000	0.99704 1.025 ^(a)	0.99568	0.99406	0.99220	0.99017
9.95	0.0221	1.02639 1.054 ^(a)	1.02427	1.02207	1.01946	1.01733
21.30	0.0525	1.06047 1.084 ^(a)	1.05764	1.05468	1.05075	1.04872
29.81	0.0798	1.08670 1.116 ^(a)	1.08355	1.08044	1.07712	1.07374
40.14	0.1207	1.11878 1.148 ^(a)	1.11505	1.11162	1.10773	1.10393
49.61	0.1677	1.14928 1.186 ^(a)	1.14559	1.14157	1.13744	1.13331
60.43	0.2381	1.18594 1.214 ^(a)	1.18124	1.17663	1.17203	1.16751
68.01	0.3031	1.21268 1.254 ^(a)	1.20772	1.20288	1.19808	1.19312
79.40	0.4410	1.25446	1.24888	1.24361	1.23846	1.23298
89.07	0.6252	1.29231	1.28665	1.28098	1.27535	1.26958

(a) D'Aprano, Goffredi and Triolo [2].

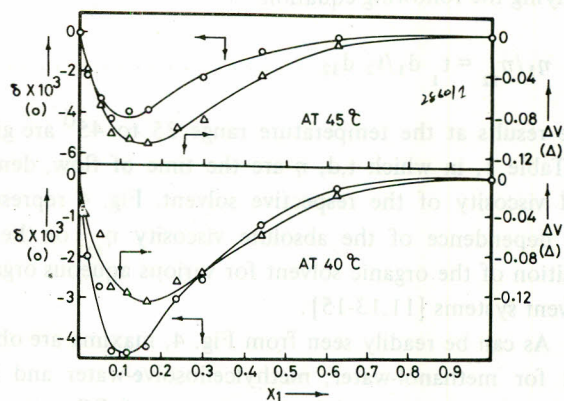


Fig. 1. Contraction in EC-water mixtures at 40° and 45°.

stabilization occurs at the concentrations corresponding 6-9 mol of water/mol of organic solute, are consistent with the stoichiometry of known clathrate hydrates [10].

Taking in consideration the explanation for the minimum in ΔV^E for alcohol-water systems which was suggested by Franks and Ives [9], the occurrence of the minimum can be attributed to competing effect on water molecule due to the polar and nonpolar ends of the organic solvent molecules.

The occurrence of the minimum in ΔV^E vs X_1 curves was also observed for other dipolar aprotic-water systems like CH₃CN-H₂O and DMSO-H₂O [4].

Further evidence for contraction in volume for EC-H₂O mixture can be obtained by calculating the molal volumes from the relation:

$$V_{12} = \frac{\sum X_i M_i \bar{V}_i}{d_{12}}, M_1 \bar{V}_1 = \frac{V_{12} - X_2 M_2 \bar{V}_2^0}{X_1} \quad \text{and}$$

$$M_2 \bar{V}_2 = \frac{V_{12} - X_1 M_1 \bar{V}_1^0}{X_2} \quad \dots \dots \dots (4)$$

where, V_{12} is the molal volume of the mixture, \bar{V}_1 is the partial molal volume of the component 1 or 2 in the mixture, \bar{V}_1^0 is the molal volume of the pure component. The variation of such partial molal volumes together with the difference $M_1 \bar{V}_1 - M_1 \bar{V}_1^0 = \Delta \bar{V}_1$ and $M_2 \bar{V}_2 - M_2 \bar{V}_2^0 = \Delta \bar{V}_2$ with X_1 or X_2 are illustrated in Fig. 2 and 3. The results gave evidence that the contraction occurs not only in the total volume of the mixture but also in the volume of each component.

2. Viscosity of binary liquid systems. The absolute viscosities of EC-H₂O mixtures were measured using Ubelohde suspended viscometer with known flow time of double distilled water at different temperatures and then applying the following equation:

$$\eta_1 / \eta_{12} = t_1 d_1 / t_2 d_{12} \quad \dots \dots \dots (5)$$

The results at the temperature range 25 to 45° are given in Table 1, in which t, d, η are the time of flow, density and viscosity of the respective solvent. Fig. 4 represents the dependence of the absolute viscosity η_{12} on the composition of the organic solvent for various aqueous organic solvent systems [11,13-15].

As can be readily seen from Fig. 4, maxima are observed for methanol-water, methylcellosolve-water and dioxane-water systems, while in the case of EC-water and glycerol-water, η_{12} increases smoothly by increasing the organic solvent component. The presence of these maxima was attributed [11] to the variation of the water structure upon the addition of an organic solvent, since the structure collapses owing to the breaking of H-bonds in the water aggregates.

Ageno [16] explained the presence of a maximum in MeOH-H₂O system assuming that, at this concentration, all hydrogen bonds in water at the given temperature are saturated by alcohol molecules. If the alcohol concentration is further increased, the viscosity of the mixture should decrease towards that of pure methanol.

Kay *et al.* [17] obtained a maximum value for η in EtOH-H₂O mixtures (at $x_{\text{eth.}} \approx 0.25$) and suggested that the structural effect is a maximum for low ethanol concentration, and the composition corresponding to the viscosity maximum is the result of two conflicting effects much

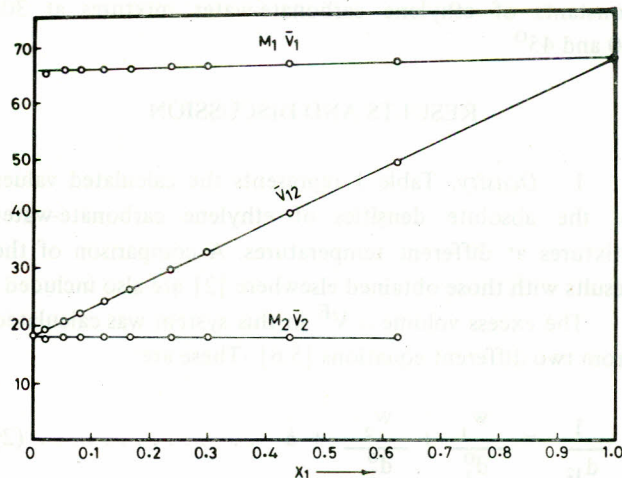


Fig. 2. Variation of $M_1 \bar{V}_1, \bar{V}_{12}, M_2 \bar{V}_2,$ and \bar{V}_{12} with X_1 at 40°.

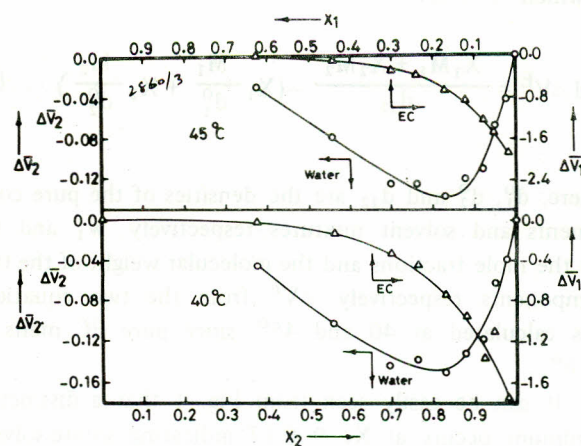


Fig. 3. Variation of $\Delta \bar{V}_1$ and $\Delta \bar{V}_2$ with mole fraction of EC at 40° and 45°.

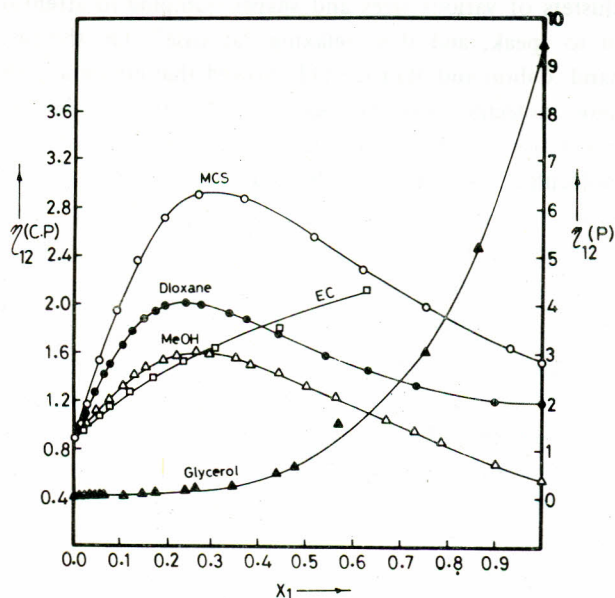


Fig. 4. Variation of absolute viscosity with composition of organic solvent.

like the maximum on the density curve of pure water.

In the case of EC-water mixtures which can form more than one independent collective hydrogen bond, the resonance transfer of molecules from one aggregate to another cannot be prevented since no saturation of the hydrogen bonds available in H₂O is obtained. This leads to a regular transition from the viscosity of the first component to that of the second.

Many attempts had been carried out to find a suitable equation which correlates the viscosity of binary mixtures with those of the components [18-23]. The conclusion drawn was that viscosity is a non-additive property and there is always deviation from linear additivity. Harms Rössler and Wolf [24] suggested the following relationship:

$$\eta_{M_{12}} = X_1 \eta_{M_1} + X_2 \eta_{M_2} \dots \dots \dots (6)$$

where, η_M is the molar viscosity, measured as a force that acts by the linear velocity gradient on a stationary plane of an area $V_M^{2/3}$ of the molar volume when it is present at a distance $V_M^{1/3}$ of the molar volume and is given by

$$\eta_M = \eta_{V_M}^{1/3} \dots \dots \dots (7)$$

The divergence from linearity $\Delta\eta_{M_{12}}$ can be calculated from the relation:

$$\Delta\eta_{M_{12}} = \eta_{calc} - \eta_{exptl} = X_1 \eta_1 V_{M_1}^{1/3} + X_2 \eta_2 V_{M_2}^{1/3} - \eta_{12} V_{M_{12}}^{1/3} \dots \dots (8)$$

The plot of $\Delta\eta_{M_{12}}$ together with η_{12} against the mole fraction of EC (Fig. 5) shows that $\Delta\eta_{M_{12}}$ has a negative value and passes through a minimum at $X_1 \approx 0.303$. This behaviour is found to be similar to that obtained in the case of methanol-carbon tetrachloride, methanol benzene [24] and methyl cellosolve-water mixtures [15] and might be interpreted on the basis of the molecular theory of internal friction due to mixing as given by Harms *et al.* [24]. According to this theory, three types of frictions were assumed: dry friction between two solid phases, inner friction between two liquid phases, and surface friction between liquid-solid phases.

3. Dielectric constant measurements. Table 3 represents the obtained values of the dielectric constant of solutions containing different amounts of ethylene carbonate at 25 [3] 30, 35, 40° and 45° together with the Debye-Hückel parameters A and B. The values of D at 25° are taken from the data obtained by D'Aprano *et al.* [3],

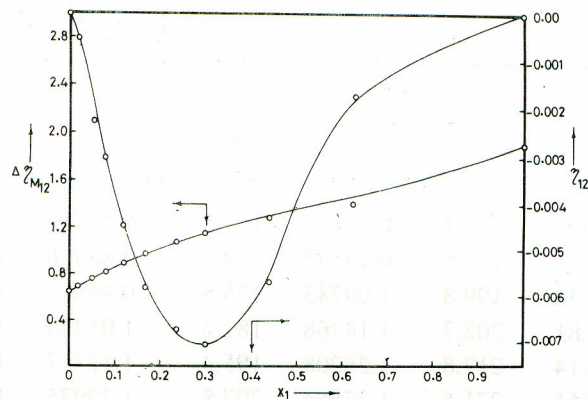


Fig. 5. Variation of η_{12} and $\Delta\eta_{M_{12}}$ with mole fraction of EC at 40°.

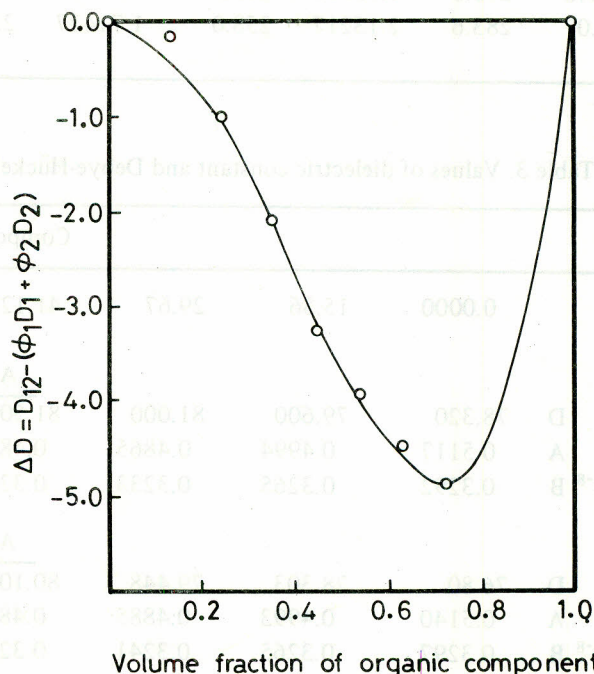


Fig. 6. Volume fraction of organic component at 40°.

and the values of D at 35° were taken by interpolation method.

The dielectric constants of EC-water mixtures are represented in Fig. 6 in terms of a deviation function, ΔD representing the deviation from an ideal volume mixture relation:

$$\Delta D = D_{12} - \phi_1 D_1 - \phi_2 D_2$$

where ϕ_1 and ϕ_2 are the volume fractions of the components based on the densities of the pure liquids. The comparison on a volume fraction basis largely compensates for the "dipole-dilution" effect discussed by Franks and Ives. [9]. It is seen that there is negative deviation from this

Table 2. Absolute viscosities at different temperatures.

EC %	25°		30°		35°		40°		45°	
	t.sec.	c.p.	t.sec.	c.p.	t.sec.	c.p.	t.sec.	c.p.	t.sec.	c.p.
Zero	172.4	0.89030	155.1	0.79750	140.8	0.71940	129.0	0.65310	188.4	0.59630
9.85	177.6	0.94195	159.7	0.83956	145.3	0.75537	132.4	0.68774	122.2	0.63211
21.30	199.8	1.09743	175.5	0.95855	158.0	0.84889	144.4	0.77421	133.4	0.71157
29.81	203.7	1.14368	182.2	1.01430	164.7	0.92803	150.5	0.82323	138.1	0.75229
40.14	217.8	1.26208	195.4	1.12517	176.3	1.00716	160.4	0.90663	147.6	0.82877
49.61	231.6	1.37864	207.8	1.22935	187.7	1.10068	171.4	0.99479	156.4	0.90155
60.43	248.4	1.52581	222.7	1.35849	201.1	1.21579	182.4	1.09083	167.3	0.99348
68.01	259.5	1.62993	231.8	1.44570	209.9	1.29492	191.3	1.16948	145.0	1.06200
79.40	270.8	1.75950	243.9	1.57301	221.6	1.41002	203.5	1.28599	186.6	1.12023
89.07	283.6	2.13217	258.0	1.71427	235.7	1.55188	216.7	1.41020	200.8	1.29666

Table 3. Values of dielectric constant and Debye-Hückel constants A and B for ethylene carbonate-water mixtures.

		Composition (%)							
		0.0000	15.36	29.67	41.12	50.90	60.04	69.04	76.65
		At 25°							
	D	78.320	79.600	81.000	81.500	82.450	83.100	84.550	85.650 ⁽³⁾
	A	0.5117	0.4994	0.4865	0.4821	0.4738	0.4682	0.4562	0.4475
10 ⁻⁸	B	0.3292	0.3265	0.3233	0.3227	0.3208	0.3196	0.3168	0.3148
		At 30°							
	D	76.80	78.303	79.448	80.100	80.802	81.503	82.975	83.795
	A	0.5140	0.4993	0.4885	0.4826	0.4763	0.4702	0.4577	0.4510
10 ⁻⁸	B	0.3297	0.3265	0.3241	0.3228	0.3214	0.3200	0.3172	0.3156
		At 35°							
	D	75.210	76.850	77.800	78.600	79.250	79.900	81.000	82.000
	A	0.5175	0.5010	0.4919	0.4844	0.4785	0.4726	0.4630	0.4546
10 ⁻⁸	B	0.3304	0.3269	0.3249	0.3232	0.3219	0.3206	0.3184	0.3164
		At 40°							
	D	73.800	75.596	76.603	77.147	77.453	78.253	79.221	80.150
	A	0.5197	0.5013	0.4915	0.4863	0.4834	0.4760	0.4673	0.4592
10 ⁻⁸	B	0.3309	0.3269	0.3248	0.3236	0.3230	0.3213	0.3194	0.3175
		At 45°							
	D	71.750	73.699	74.736	75.398	76.119	76.702	77.452	78.263
	A	0.5294	0.5086	0.4980	0.4915	0.4845	0.4790	0.4720	0.4647
10 ⁻⁸	B	0.3329	0.3285	0.3262	0.3248	0.3232	0.3220	0.3204	0.3185

linear relation, which indicates changes in the degree of alignment of dipoles with change of position. Reynaud [25] obtained negative deviation in ΔD for monoalkylated amide-water mixtures and explained the results on the assumption that amide-amide hydrogen bonds are broken by the addition of water.

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