sions and for the generous supply of substrate and other chromatographic items.

## Glossary

| | |
|---|---|
| $a_1$ | activity of solvent in polymer solution |
| $B_{11}$ | second virial coefficient of pure solvent, $cm^3/(g\text{-}mol)$ |
| $f_1^\circ$ | fugacity of pure solvent at system $T$ and reference pressure, atm |
| $f_p$ | pressure correction term |
| $\Delta H_s$ | heat of solution, kcal/mol |
| $M_i$ | molecular weight of component i |
| $M_n$ | number average molecular weight |
| $M_w$ | weight average molecular weight |
| $P_1$ | partial pressure of the solvent, atm |
| $P_1^s$ | saturation vapor pressure of the solvent, atm |
| $P_i$ | column inlet pressure, psig |
| $P_o$ | column outlet pressure, psig |
| $Q$ | flow rate at column outlet pressure and temperature, $cm^3/min$ |
| $R$ | universal gas constant, 82.056 $cm^3$ atm/(g-mol K) |
| $r$ | ratio of molecular volumes of polymer to solvent |
| $T$ | system temperature, K |
| $t$ | system temperature, °C |
| $t_g$ | residence time of the solvent, min |
| $t_r$ | residence time of air, min |
| $V_1$ | molar volume of liquid solvent at saturation, $cm^3$/g-mol |
| $V_g$ | specific retention volume, $cm^3/g$ |
| $V_g^0$ | specific retention volume corrected to 0 °C, $cm^3/g$ |
| $W_2$ | weight of polymer in column, g |
| $x_1$ | liquid mole fraction of solvent |
| $y_1$ | vapor mole fraction of solvent |
| $\gamma_1$ | mole fraction activity coefficient of solvent |
| $\gamma_1^\infty$ | mole fraction activity coefficient of solvent at infinite dilution |
| $\rho_i$ | mass density of component $i$, $g/cm^3$ |
| $\phi_1$ | vapor-phase fugacity coefficient of solvent |
| $\phi_1^s$ | fugacity coefficient of solvent at saturation pressure |
| $\Phi_i$ | volume fraction of component $i$ |
| $\chi$ | Flory–Huggins parameter |
| $\Omega_1^\infty$ | weight fraction activity coefficient of solvent at infinite dilution |

**Registry No.** PS, 9003-53-6; PBD, 9003-17-2; PIP, 9003-31-0; cyclohexane, 110-82-7; benzene, 71-43-2; toluene, 108-88-3; hexane, 110-54-3; ethylbenzene, 100-41-4; chloroform, 67-66-3; carbon tetrachloride, 56-23-5; *p*-xylene, 106-42-3; methylene chloride, 75-09-2; 1,2-dichloroethane, 107-06-2; *n*-butylbenzene, 104-51-8; methyl isobutyl ketone, 108-10-1; cyclohxanone, 108-94-1; *N*,*N*-dimethylformamide, 68-12-2; tetrahydrofuran, 109-99-9; acetone, 67-64-1; acetonitrile, 75-05-8; methanol, 67-56-1; isopropyl alcohol, 67-63-0; butyl alcohol, 71-36-3; benzyl alcohol, 100-51-6; ethyl acetate, 141-78-6; methyl ethyl ketone, 78-93-3; benzaldehyde, 100-52-7; aniline, 62-53-3; acetic acid, 64-19-7; ethylene glycol, 107-21-1.

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# Excess Properties of the Binary Liquid System Propylene Carbonate + Acetonitrile

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**Dielectric constants, densities, viscosities, and refractive indices for the propylene carbonate + acetonitrile system were determined over the entire composition range of the system and at various temperatures, ranging from 25 to 45 °C. Excess dielectric constants, excess volumes, excess viscosities, and excess Gibbs energies of activation of the viscous flow, as well as Kirkwood correlation factors, have been calculated and studied. Their behavior strongly suggests the existence of intermolecular interactions.**

## Introduction

Several previous papers (*1*, *2*) from our laboratory have been concerned with the physical and thermodynamic properties of binary liquid systems of technological interest. Here we report excess properties of the propylene carbonate (PC) + acetonitrile (AN) system. Although both components of the system have a wide range of technological applications, namely, in battery systems and plating techniques (*3*, *4*), it appears that their binary system has not been studied. We thus carried out measurements on the dielectric constants, viscosities, densities, and refractive indices over the entire mole fraction range of the system at 25, 30, 35, 40, and 45 °C. By means of the experimental results, the relevant excess functions as well as the Kirkwood correlation factor ($g_k$) have been evaluated since their study may lead to conclusions concerning the deviation of the system from an ideal mixture behavior.

## Experimental Section

Propylene carbonate (Merck zur synthese 99%) was dried over 4A molecular sieves and fractionally distilled under vacu-

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um. The middle fraction was collected. The value of specific conductance was less than $10^{-8}$ $\Omega^{-1}$ cm$^{-1}$. Acetonitrile (Merck p.a.) was dried over 3A molecular sieves and distilled, and the middle fraction was collected. Its specific conductance was less than $5 \times 10^{-8}$ $\Omega^{-1}$ cm$^{-1}$.

Dielectric constants were measured with a dipolemeter (Model WTW DM-01, Wissenschaftlich Technische Werkstatten GmbH). The cell was thermostated (±0.02 °C). The reproducibility of the measurements was approximately equal to 0.2 unit of dielectric constant.

Refractive indices were measured by means of a thermostated (±0.2 °C) Abbe refractometer. The reproducibility was ±0.0001 unit. Values were obtained for Na D light.

Viscosity measurements were carried out by means of an Ubbelohde suspended-level viscometer. Flow times were measured to ±0.01 s with an electronic stopwatch. Kinetic energy corrections were applied to the viscosity data. Temperature control during the viscosity measurements was ±0.01 °C. The reproducibility in viscosity was ±50 μPa s.

Densities were measured with a Sprengel-Ostwald pycnometer having a volume of about 25 mL. The temperature control had an accuracy of ±0.01 °C; the reproducibility was $\pm 5 \times 10^{-5}$ g/cm$^3$.

## Results

The experimental results of dielectric constants, viscosities, refractive indices, and densities are reported in Table I.

The excess functions, namely, excess dielectric constant $\epsilon^E$, excess viscosity $\eta^E$, excess volume $V^E$, and excess Gibbs energy of activation of flow $G^{*E}$, were calculated by using the following equations:

$$\epsilon^E = \epsilon - (\epsilon_1 x_1 + \epsilon_2 x_2) \tag{1}$$

$$\eta^E = \eta - (\eta_1 x_2 + \eta_2 x_2) \tag{2}$$

$$V^E = V - (V_1 x_1 + V_2 x_2) \tag{3}$$

$$G^{*E} = RT[\ln(\eta V) - (x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2))] \tag{4}$$

where $x_1$ and $x_2$ are the mole fractions, $\epsilon$, $\epsilon_1$, and $\epsilon_2$ are the dielectric constants of the mixture and of the pure components, and $\eta$, $\eta_1$, and $\eta_2$ are the viscosities of the mixture and of the pure components, respectively. The molar volume $V$ is defined by the relationship

$$V = (x_1 M_1 + x_2 M_2)/d \tag{5}$$

where $M_1$ and $M_2$ are the molecular weights of the pure substances and $d$ is the mass density.

The Kirkwood correlation factor $g_k$ is given by the expression (*5, 6*)

$$g_k = \frac{(\epsilon - \epsilon_0)(2\epsilon - \epsilon_0)}{\epsilon(\epsilon_0 + 2)^2} \frac{9kT}{4\pi N d} \frac{M_1 x_1 + M_2 x_2}{(\mu_1 x_1 + \mu_2 x_2)^2} \tag{6}$$

where $\epsilon$ is the static dielectric constant, $\epsilon_0$ is the dielectric constant at high frequency, $N$ is Avogadro's number, $k$ is Boltzmann's constant, and $\mu_i$ is the dipole moment of the $i$th substance.

Throughout the calculations, the following values for the pure substances were used: $\mu$(PC) = 4.94 D and $\mu$(AN) = 3.44 D. The $\epsilon_0$ was set equal to $1.1n^2$ where $n$ is the refractive index of the mixture.

## Discussion

The dielectric constant and the related properties are correlated to some extent with the local structure of the liquid. Experimental values of the static dielectric constant of pure propylene carbonate have been reported by several workers. Our measured value ($\epsilon$ = 65.16 at 25 °C) is in good agreement with that proposed by Payne and Theodorou (*7*), Fuoss and Hirsch (*8*), and Watanabe and Fuoss (*9*) at the same temperature.

**Table I. Experimental Dielectric Constant ($\epsilon$), Refractive Index ($n$), Density ($\rho$, g/cm$^3$), and Viscosity ($\eta$, μPa s): Data for the Propylene Carbonate–Acetonitrile Mixtures at 25, 30, 35, 40, and 45 °C**

| $x$(PC) | $\epsilon$ | $n$ | $\rho$ | $\eta$ |
|---|---|---|---|---|
| | | At 25 °C | | |
| 0.0000 | 35.99 | 1.3416 | 0.7759 | 344 |
| 0.0418 | 37.32 | 1.3481 | 0.8067 | 383 |
| 0.0892 | 39.89 | 1.3549 | 0.8379 | 423 |
| 0.1438 | 42.05 | 1.3622 | 0.8736 | 479 |
| 0.2071 | 44.0 | 1.3695 | 0.9105 | 551 |
| 0.2815 | 47.048 | 1.3766 | 0.9503 | 642 |
| 0.3701 | 49.90 | 1.3846 | 0.9938 | 778 |
| 0.4776 | 53.03 | 1.3923 | 1.0387 | 968 |
| 0.6104 | 56.63 | 1.4020 | 1.0882 | 1248 |
| 0.7791 | 60.67 | 1.4106 | 1.1401 | 1675 |
| 1.0000 | 65.16 | 1.4194 | 1.1995 | 2512 |
| | | At 30 °C | | |
| 0.0000 | 35.24 | 1.3397 | 0.7717 | 328 |
| 0.0418 | 37.07 | 1.3457 | 0.8011 | 363 |
| 0.0892 | 39.15 | 1.3525 | 0.8346 | 403 |
| 0.1438 | 41.23 | 1.3603 | 0.8681 | 454 |
| 0.2071 | 43.53 | 1.3676 | 0.9052 | 521 |
| 0.2815 | 46.13 | 1.3745 | 0.9448 | 605 |
| 0.3701 | 49.07 | 1.3827 | 0.9886 | 731 |
| 0.4776 | 52.12 | 1.3827 | 1.0333 | 906 |
| 0.6104 | 55.65 | 1.3906 | 1.0826 | 1161 |
| 0.7791 | 59.54 | 1.3998 | 1.1355 | 1535 |
| 1.0000 | 64.13 | 1.4174 | 1.1941 | 2300 |
| | | At 35 °C | | |
| 0.0000 | 34.54 | 1.3369 | 0.7662 | 314 |
| 0.0418 | 36.36 | 1.3429 | 0.7961 | 347 |
| 0.0892 | 38.43 | 1.3503 | 0.8292 | 384 |
| 0.1438 | 40.45 | 1.3574 | 0.8630 | 432 |
| 0.2071 | 42.76 | 1.3650 | 0.8998 | 494 |
| 0.2815 | 45.34 | 1.3724 | 0.9396 | 575 |
| 0.3701 | 48.29 | 1.3806 | 0.9834 | 693 |
| 0.4776 | 51.32 | 1.3885 | 1.0280 | 846 |
| 0.6104 | 54.70 | 1.3979 | 1.0774 | 1078 |
| 0.7791 | 58.48 | 1.4066 | 1.1301 | 1420 |
| 1.0000 | 63.07 | 1.4155 | 1.1887 | 2080 |
| | | At 40 °C | | |
| 0.0000 | 33.85 | 1.3342 | 0.7609 | 301 |
| 0.0418 | 35.67 | 1.3409 | 0.7909 | 331 |
| 0.0892 | 37.77 | 1.3480 | 0.8238 | 367 |
| 0.1438 | 39.78 | 1.3551 | 0.8589 | 411 |
| 0.2071 | 42.13 | 1.3631 | 0.8945 | 469 |
| 0.2815 | 44.60 | 1.3704 | 0.9338 | 543 |
| 0.3701 | 47.55 | 1.3785 | 0.9782 | 654 |
| 0.4776 | 50.29 | 1.3864 | 1.0229 | 802 |
| 0.6104 | 53.69 | 1.3963 | 1.0723 | 1054 |
| 0.7791 | 57.46 | 1.4045 | 1.1250 | 1310 |
| 1.0000 | 61.94 | 1.4193 | 1.1836 | 1902 |
| | | At 45 °C | | |
| 0.0000 | 33.12 | 1.3314 | 0.7559 | 289 |
| 0.0418 | 35.15 | 1.3383 | 0.7856 | 316 |
| 0.0892 | 37.31 | 1.3457 | 0.8187 | 353 |
| 0.1438 | 39.28 | 1.3532 | 0.8529 | 397 |
| 0.2071 | 41.507 | 1.3610 | 0.8894 | 455 |
| 0.2815 | 43.89 | 1.3682 | 0.9294 | 509 |
| 0.3701 | 47.06 | 1.3762 | 0.9731 | 625 |
| 0.4776 | 49.06 | 1.3844 | 1.0183 | 760 |
| 0.6104 | 52.79 | 1.3947 | 1.0671 | 965 |
| 0.7791 | 56.47 | 1.4026 | 1.1176 | 1220 |
| 1.0000 | 60.92 | 1.4113 | 1.1783 | 1755 |

The excess dielectric constant gives an estimate of dipole-dipole interactions and hydrogen-bonded complexes. The excess dielectric constant–composition data for the binary liquid system propylene carbonate–acetonitrile at 25 °C are plotted

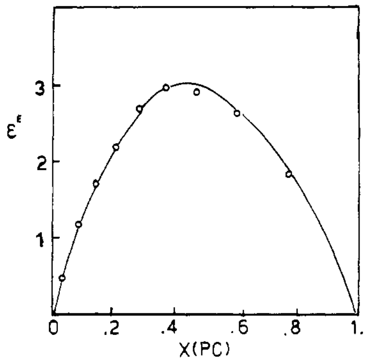

**Figure 1.** Variation of the excess dielectric constant with the mole fraction of propylene carbonate at 25 °C.

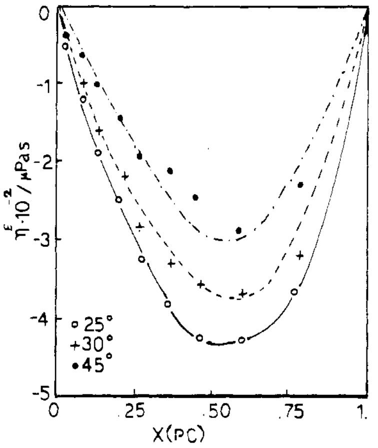

**Figure 2.** Variation of the excess viscosity with the mole fraction of propylene carbonate at 25, 30, and 45 °C.

in Figure 1. The $\epsilon^E$ remains positive through the whole composition range. The calculated values of $\epsilon^E$ show that there are no considerable changes on $\epsilon^E$ over the temperature range studied (25-45 °C). The curve $\epsilon^E$ vs mole fraction $x$ presents a maximum at mole fraction $x = 0.5$.

The excess viscosity gives an estimate of intermolecular interactions. The system propylene carbonate-acetonitrile shows negative deviations of $\eta^E$ from ideality over the entire mole fraction range and over the whole range of studied temperatures. The minimum corresponds to 0.5 mole fraction, Figure 2. As the temperature increases, the magnitude of the excess volume decreases, i.e., becomes less negative, showing a tendency to ideal behavior. According to Ford and Moore (*10*), negative values of $\eta^E$ occur for systems of different molecular sizes, and the dispersion forces are primarily responsible for the interactions.

The $V^E$ values appear to be negative over the entire range of concentration, as shown in Figure 3, and become more negative as the temperature increases. The minimum lies at a mole fraction of about 0.5. The position of this minimum can be explained, assuming that there are dispersion forces between the different kinds of molecules of the liquid and that a stable complex consisting of one molecule of propylene carbonate and one molecule of acetonitrile is formed. This model is in accordance with the Prigogine (*11*) theory, which attributes the negative $V^E$ values to different sizes of molecules or to the dipole-dipole interaction between them.

With regard to this complex formation, it seems to be in favor with a temperature increase. The same phenomenon has been also observed in systems in which one of the components is acetonitrile or generally a nitrile (*13*, *14*).

Another thermodynamic function, which is investigated, is the excess free energy of activation of flow ($G^{*E}$). The values of $G^{*E}$ were calculated from eq 4, which results from the Eyring equation for viscosity flow modified for a binary mixture. Figure 4 shows the variation of $G^{*E}$ as a function of mole fraction. The values of $G^{*E}$ are always positive, and the maximum appears at a mole fraction of about 0.5.

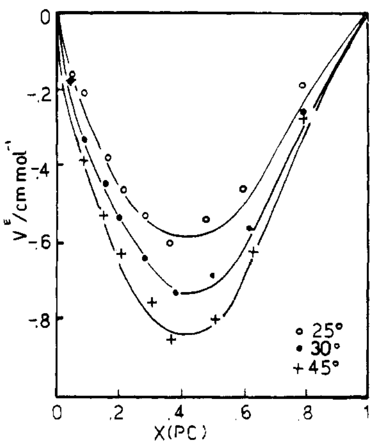

**Figure 3.** Variation of the excess volume with the mole fraction of propylene carbonate at 25, 30, and 45 °C.

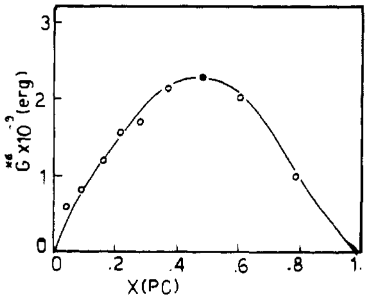

**Figure 4.** Variation of $G^{*E}$ with the mole fraction of propylene carbonate at 25 °C.

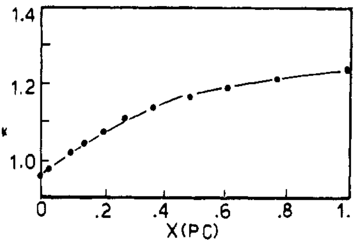

**Figure 5.** Variation of the Kirkwood factor with the mole fraction of propylene carbonate at 25 °C.

The influence of the temperature is not significant. As is shown in Figure 4, changes of temperature between 25 and 45 °C do not have any affect, within experimental errors, on $G^{*E}$.

Another important parameter, which has also been taken into account in this work, is the Kirkwood correlation factor, $g_K$. This parameter provides useful information regarding the molecule orientation hindrance that, in turn, is indicative of the existence and/or of the extent of short range type intermolecular interactions in the liquid. For the system under study, $g_K$ values have been calculated by means of eq 6, a modified form of the Kirkwood-Cole (*5*) equation so that it is applicable to a binary mixture. Note that $\epsilon_0$ was taken equal to $1.1n^2$, where $n$ is the refractive index; it is also accepted that the dipole moments are not temperature-dependent throughout the calculations. Figure 5 represents the variation of $g_K$ of the system with the PC concentration. As can be seen, $g_K$ values increase rapidly up to a mole fraction of about 0.5 and slightly thereafter with increasing PC concentration. It is also worth noting that all derived $g_K$ values are not far from unity (0.996-1.25 at 25 °C) over the entire mole fraction range. This fact suggests that there must be a lack of specific intermolecular forces in the mixture and pure components while strong dipole–dipole forces predominate. With regard to the pure components, the deviations from Trouton's constant (a value higher than 21), their high boiling points, and the weak temperature dependence of their $g_k$ values (0.986 for PC and 1.26 for AN at 45 °C) seem to support the observation stated above.

### Glossary

| | |
|---|---|
| $\epsilon^E$ | excess dielectric constant |
| $\eta^E$ | excess viscosity |
| $V^E$ | excess molar volume |
| $x$ | mole fraction |
| $d$ | density |
| $n$ | refractive index |
| $G^{*E}$ | excess free energy of activation of the flow |

**Registry No.** PC, 108-32-7; AN, 75-05-8.

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# Vapor–Liquid Equilibria for the Systems Carbon Dioxide–Ethylbenzene and Carbon Dioxide–Styrene

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**Vapor–liquid equilibrium data were measured for the systems $CO_2$–ethylbenzene and $CO_2$–styrene over a pressure range from 14 to 85 atm at 308, 318, and 328 K. Vapor–liquid equilibrium data were also measured over the same pressure and temperature ranges for the system $CO_2$–ethylbenzene–styrene, where the ratio of styrene to ethylbenzene in the liquid phase was kept at 1.86.**

## Introduction

Styrene is an important petrochemical raw material that is commonly produced by dehydrogenation of ethylbenzene (EB). Because of incomplete reaction, vacuum distillation is generally employed to separate these two compounds from the effluent stream, containing about 65% styrene and 35% EB. Due to the extensive energy required for vacuum distillation, use of liquid or supercritical $CO_2$ as a solvent to separate styrene and EB may be an alternative separation method. In order to determine if this is the case, phase equilibrium data for $CO_2$–styrene and $CO_2$–EB are needed. Although the equilibrium data for several $CO_2$–aromatic $C_7$ or $C_8$ systems have been reported in the literature (*1–4*), the data for these two systems do not appear to be available. In this work the vapor–liquid equilibrium data for these two systems and for the system $CO_2$–styrene–EB over the pressure range from 14 to 85 atm at 308, 318, and 328 K are reported.

## Experimental Section

The experimental apparatus used in this work is illustrated in Figure 1. The entire apparatus was constructed with 0.63-cm-o.d. stainless steel 316 tubing, except the equilibrium cells. EB was purchased from Merck Co. with a minimum purity of 99.9%. Styrene was supplied by Taiwan Styrene Monomer Corp., with a claimed purity of 99+%, and contained 3 ppm of inhibitor 4-*tert*-butylcatechol, as received. Both chemicals were used without further purification. The first equilibrium cell, having a diameter of 2.54 cm, was filled with about 120 mL of styrene, EB, or styrene + EB. In order to prevent entrainment, several layers of glass beads supported by a perforated stainless steel disk were placed at the top of the cell. To assure saturation, a second equilibrium cell was also employed. However, the data indicated that a single cell was enough when the flow rate of the gas after expansion was less than 30 mL/min. This value was also observed to be the maximum flow rate allowed to obtain the equilibrium data. The equilibrium cells were immersed in a constant-temperature bath, which could be controlled to within ±0.5 K.

The experiment started with the compression of $CO_2$ (minimum purity of 99.8%) into a surge tank by a diaphragm compressor (Superpressure Inc.). In each experiment the pressure could be maintained to within ±10 psi of the desired value. A preheating coil was used to ensure that the carbon dioxide reached the temperature of the bath. The gas coming from the equilibrium cells was expanded across a metering valve, which was wrapped with heating tape. The condensed styrene, EB, or styrene + EB was collected in a cold trap, containing 400 mL of alcohol. The cold trap was surrounded by a mixture of salt and ice at about −10 °C. Samples of 4.8 μL were sent to a flame ionization detector gas chromatograph (Varian 3700) for composition analysis. To assure that all the hydrocarbons coming from the equilibrium cells can be collected, two cold traps in series were used in the preliminary runs. However, it was found that only one cold trap was needed since no hydrocarbons could be detected in the second cold trap and in the effluent gas stream. The total amount of $CO_2$ passed through the equilibrium cells was determined by measuring the volume of the expanded gas as it passed through a cold trap and a wet test meter. To eliminate possible measurement error, liquids in the cold trap and in the wet test meter were saturated with carbon dioxide first, which was done by passing the pure carbon dioxide through them before each experiment. The composition in the gas phase could be determined from the measured amounts of condensed solute and $CO_2$. At least ten

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