Several Properties of Acetonitrile-Water, Acetonitrile-Methanol, and Ethylene Carbonate–Water Systems

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Dielectric constants, viscosities, and densities for acetonitrile-water and acetonitrile-methanol mixtures have been determined at 25° C. Viscosities, refractive indices, and densities at 25° C., as well as freezing point data, are reported for ethylene carbonate–water mixtures. Where possible, the data are compared with previously reported values. Molar polarizations for the acetonitrile mixtures are shown to be linear functions of the weight per cent through the complete range of solvent mixtures.

THE DATA presented here were accumulated during the course of an extensive investigation (*6*, *7*) of the transport properties of electrolytes in a number of solvents and solvent mixtures.

EXPERIMENTAL

The dielectric constants were measured by the bridge method (General Radio Type 1615-A conductance-capacitance transformer ratio-arm bridge) using completely shielded cells fitted with well-guarded electrodes. The cells consist essentially of concentric borosilicate glass cylinders containing platinum film electrodes fused onto the appropriate glass surfaces (*11*). All cell constants were measured directly with the cell containing dry nitrogen and calculated from $C_0 = C_{N_2}/1.0005$. Two cells with C_0 equal to 2.2 and 8.78 picofarads were used, with the latter attached to a 500-ml. Erlenmeyer flask to facilitate measurements on the solvent mixtures. Solvent could be added from a weight buret under nitrogen, and N_2 pressure could be used to pump the liquid in and out of the dielectric cell. Both dielectric cells gave indistinguishable results. A correction was applied to the data to compensate for the effective capacitance associated with the resistance network used to balance the solvent conductances. The magnitude of this correction was determined from measurements on samples of water with successively increasing conductance (*10*). A very small correction ($<0.1\%$) was made for electrode polarization as determined from the frequency dependence of the measured capacitances.

Single-capillary, 25-ml. pycnometers, in which the liquid was allowed to rise into a dry capillary, were used for the density measurements.

An Ubbelohde-type suspended-level viscometer with a flow time of 500 seconds for water at 25° C. was employed for all viscosity measurements. No kinetic energy correction was necessary. The calibrating liquids used were *n*-decane and *n*-hexane, which in turn were based on the water value, η (H_2O, 25° C.) = 0.008903 poise.

Temperature regulation at 25° ± 0.001° C. for the above measurements was obtained in a thermostatically controlled water bath with the absolute temperature determined by a calibrated platinum resistance thermometer. All solvent mixtures were made up by weight and vacuum corrected.

The refractive indices of the ethylene carbonate mixtures at 25° ±0.1° C. were measured on a Bausch and Lomb Abbé Refractometer using the Na 5893-A. line.

Acetonitrile was purified by the procedure described by Coetzee *et al.* (*4*) with the addition of a final fractional distillation under nitrogen from calcium hydride through a 1.2-meter Stedman column. The final product had a specific conductance of 3 to 9×10^{-8} ohm^{-1} cm.$^{-1}$

Methanol was purified by the procedure of Kay, Zawoyski, and Evans (*8*). Distilled water was further purified by passage through a mixed bed ion exchange resin.

Ethylene carbonate was fractionally distilled at 110° C. and 8 mm. of Hg pressure and fractionally crystallized to give a pure white product that melted sharply at 36.3° C., in good agreement with Seward's value of 36.4° C. (*9*).

RESULTS

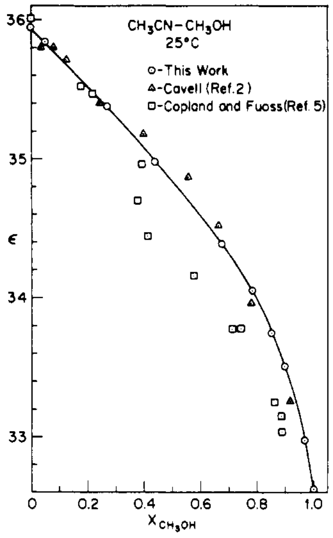
The data for the acetonitrile-methanol mixtures are given in Table I at various mole fractions of methanol. The accuracy of all the dielectric and viscosity data is estimated to be 0.1% and that of the densities, to be 0.01%. The dielectric data are plotted in Figure 1 as a function of the mole fraction methanol and are compared with data reported by Coplan and Fuoss (*5*) and Cavell *et al.* (*3*). The data of the latter workers as published were in poor agreement with our own for the acetonitrile-rich mixtures. This was due to the fact that they fitted their data to the equation $C_{\text{obsd.}} = \epsilon C_0 + C'$ using ϵ (CH_3OH) = 32.63 and ϵ (CH_3CN) = 36.69 to determine the two constants C_0 and C'. When they set ϵ (CH_3CN) equal to our value,

Table I. Experimental Dielectric Constants, Viscosities, and Densities of Acetonitrile-Methanol Mixtures at 25° C.

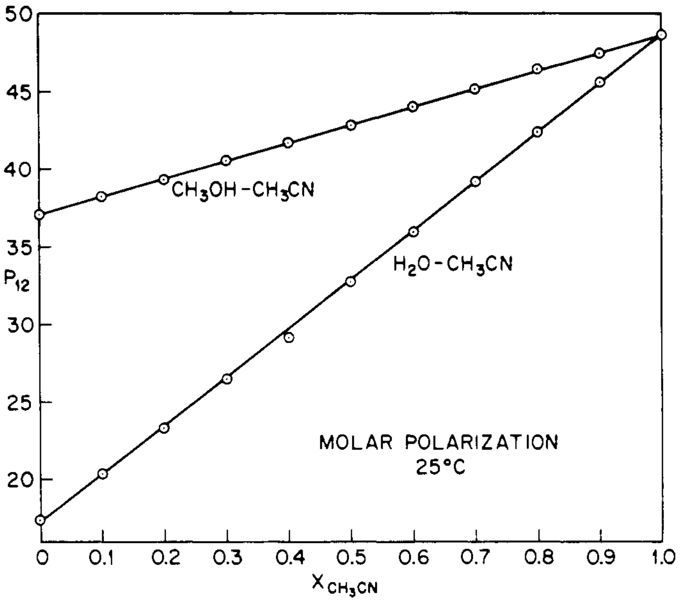
X_{CH_3OH}	ϵ	X_{CH_3OH}	$10^2\eta$, Poise	ρ, G. Ml.$^{-1}$
0.0000	35.95	0.0000	0.340_9	0.77670
0.0510	35.84	0.1219	0.331_2	. . .
0.2689	35.38	0.2160	0.329_6	. . .
0.4390	34.98	0.3487	0.334_8	. . .
0.6767	34.39	0.6804	0.339_8	. . .
0.7823	34.05	0.8910	. . .	0.78700
0.8490	33.75	0.9000	0.480_6	0.78703
0.8977	33.51	1.000	0.542_8	0.78658
0.9677	32.98	. . .	. . .	. . .
1.0000	32.62	. . .	. . .	. . .

Table II. Experimental Dielectric Constants, Densities, and Viscosities of Acetonitrile-Water Mixtures at 25° C.

X_{H_2O}	ϵ	X_{H_2O}	$10^2\eta$, Poise	X_{H_2O}	ρ, G. Ml.$^{-1}$
0.0000	35.95	0.0000	0.340_9	0.0000	0.7767
0.0075	36.03	0.2626	0.420_2	0.0441	0.7806
0.0462	36.62	0.4466	0.517_1	0.1010	0.7862
0.1331	38.10	0.4952	0.554_5	0.2000	0.7977
0.2350	40.05	0.6032	0.651_4	0.3283	0.8155
0.3709	43.18	0.6130	0.660_6	0.6197	0.8707
0.5767	49.89	0.6508	0.669_7	0.8177	0.9275
0.7569	59.25	0,7029	0.754_5	1.0000	0.9971
0.8243	64.01	0.7445	0.801_0	. . .	. . .
0.9166	71.85	0.7543	0.815_1	. . .	. . .
0.9657	75.87	1.0000	(0.8903)	. . .	. . .
0.9797	76.91	. . .	. . .	. . .	. . .
0.9976	78.15	. . .	. . .	. . .	. . .
1.0000	78.35	. . .	. . .	. . .	. . .



◀ Figure 1. Dielectric constant of acetonitrile-methanol mixtures at 25° C.



▶ Figure 2. Molar polarization of acetonitrile-methanol (top) and acetonitrile-water (bottom) mixtures at 25° C.

the agreement with our data over the whole range of solvent temperatures is good (*2*). The present authors' value of ϵ (CH$_3$CN) = 35.95 is in good agreement with the value quoted by Coplan and Fuoss (*5*). This lower value compared to that originally used by Cavell *et al.* (*3*) is due, we believe, to the better purification procedure to which our acetonitrile was subjected. The authors were unable to reproduce the 0.0015 increase in density observed by Cavell *et al.* (*3*) on adding about 10% acetonitrile to methanol, but obtained only about one fourth as large an increase, and our values of ρ are very close to those reported by Coplan and Fuoss (*5*). These viscosity data are also in good agreement with those of Coplan and Fuoss (*5*), except that our values for acetonitrile and the acetonitrile-rich mixtures are about 1.2% lower.

The data for acetonitrile-water and ethylene carbonate-water mixtures at 25° C. are given in Tables II and III. Table IV contains the freezing points for ethylene carbonate-water mixtures.

Table III. Experimental Viscosities, Densities, and Refractive Indices of Ethylene Carbonate-Water Mixtures at 25° C.

X_{EC}	$10^2\ \eta$, Poise	X_{EC}	ρ, G. Ml.$^{-1}$	X_{EC}	n
0.0	(0.8903)	0.0	0.9971	0.0	1.3325
0.0166	0.955_8	0.02206	1.0264	0.0222	1.3406
0.0221	0.968_1	0.04865	1.0566	0.0406	1.3462
0.0415	1.038	0.08061	1.0873	0.0813	1.3568
0.0635	1.096	0.11984	1.1183	0.1188	1.3650
0.0897	1.172	0.16790	1.1496	0.1760	1.3755
0.1194	1.253	0.23303	1.1836	0.2202	1.3812
0.1403	1.309	0.32230	1.2194	0.2734	1.3875
0.1625	1.377	0.44231	1.2546	0.3107	1.3914
0.2345	1.519	0.64483	1.2954	0.3839	1.3977
0.3229	1.647	1.0000^a	1.3383^a	0.4224	1.4007
0.3784	1.704	...	...	0.4657	1.4035
0.4412	1.751	...	...	0.5214	1.4069
0.5409	1.831	...	...	0.5777	1.4094
0.6443	1.898	...	...	0.6660	1.4137

^{a} Supercooled.

Table IV. Experimental Freezing Points of Ethylene Carbonate-Water Mixtures

EC, Wt. %	*FP*, ° C.	EC, Wt. %	*FP*, ° C.	EC, Wt. %	*FP*, ° C.
10.0	-2.0	62.3	21.5	91.6	25.4
15.0	3.9	70.5	21.7	94.0	26.6
20.0	9.6	75.2	22.1	94.4	26.6
25.0	14.2	84.5	23.0	96.7	29.2
30.0	16.9	85.0	23.0	97.0	29.5
41.2	19.2	89.1	24.0	98.2	31.8
46.3	20.6	89.6	24.3	100.0	36.3
50.5	20.7	...	...	...	...

DISCUSSION

One distinctive feature of these mixtures of acetonitrile with hydrogen bonding solvents is that the molar polarization calculated from

$$P_{12} = \frac{(\epsilon - 1)}{(\epsilon + 2)} \frac{(X_1M_1 + X_2M_2)}{\rho} \qquad (1)$$

is linear in the mole fraction acetonitrile through the whole range of solvent compositions, as shown in Figure 2. On the other hand, mixtures of acetonitrile with the nonhydrogen-bonding solvent, carbon tetrachloride, can be shown (*1*) to have a completely nonlinear molar polarization curve containing a very pronounced maximum. This does not imply that the acetonitrile mixtures studied here can be considered ideal noninteracting mixtures. The viscosities, densities, and dielectric constants show large deviations from the values calculated by assuming additivity of the properties of the pure components.

NOMENCLATURE

C = capacitance, picofarads
EC = ethylene carbonate
FP = freezing point, ° C.
M = molecular weight
n = refractive index
P_{12} = molar polarization
X = mole fraction
ϵ = dielectric constant
ρ = density, g. ml.$^{-1}$
η = viscosity, poise

LITERATURE CITED

(1) Berns, D.S., Fuoss, R.M., *J. Am. Chem. Soc.* **83**, 1321 (1961).
(2) Cavell, E.A.S., University of Southampton, England, private communication, 1965.
(3) Cavell, E.A.S., Jerrard, H.G., Simmonds, B.A.W., Speed, J.A., *J. Phys. Chem.* **69**, 3657 (1965).
(4) Coetzee, J.F., Cunningham, G.P., McGuire, D.K., Padmanabhan, G.R., *Anal. Chem.* **34**, 1139 (1962).
(5) Coplan, M.A., Fuoss, R.M., *J. Phys. Chem.* **68**, 1181 (1964).
(6) Kay, R.L., Evans, D.F., *Ibid.*, **70**, 2325 (1966).
(7) Kay, R.L., Vituccio, T., Zawoyski, C., Evans, D.F., *Ibid.*, **70**, 2336 (1966).
(8) Kay, R.L., Zawoyski, C., Evans, D.F., *Ibid.*, **69**, 4208 (1965).
(9) Seward, R.P., Vieira, E.C., *Ibid.*, **62**, 127 (1958).
(10) Vidulich, G.A., Evans, D.F., Kay, R.L., *Ibid.*, **71**, 656 (1967).
(11) Vidulich, G.A., Kay, R.L., *Rev. Sci. Instr.* **37**, 1662 (1966).

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