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Dielectric Constants, Viscosities, Fusion Point Curves, and Other Properties of Three Nonaqueous Binary Systems

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Dielectric constants, viscosities, densities, refractive indices, molar excess volumes, and dielectric constant deviations are reported for *N*-methylacetamide–ethylene carbonate, *N*-methylacetamide–dimethylsulfoxide, and ethylene carbonate–dimethylsulfoxide mixtures at 40° C. Fusion point curves also have been determined for these systems.

N-methylacetamide (NMA), ethylene carbonate (EC), and dimethylsulfoxide (DMSO) are excellent electrolytic solvents which have convenient freezing points and medium cryoscopic constants. Each of these solvents can be highly purified through a series of fractional freezings or by zone refining. The useful data reported herein were accumulated in the course of physicochemical investigations dealing with pure and mixed nonaqueous media.

EXPERIMENTAL

Each solvent was purified through a sequence of fractional freezings under nitrogen (*4*) until a constant maximum freezing point (indicated in Table II) was obtained. All solutions were prepared in glass-stoppered flasks on a weight basis in sufficient quantity to permit separate portions to be used for each measurement.

A Twin-T impedance bridge assembly was used to make capacitance measurements at 1 MHz. The jacketed stainless steel cells plugged directly into the bridge. The standard media used for the determination of cell constants were air and water which have dielectric constants of unity and 73.15 (*11*), respectively, at 40° C. Size 50 or 100 Cannon-Fenske viscometers were used to obtain efflux times of 200 sec or more thereby making kinetic energy corrections negligible. Calibration data for the viscometers were provided by the Cannon Instrument Co. To minimize atmospheric contamination, the viscometers were equipped with top adapters vented through tubes filled with calcium chloride and Ascarite. Timers were calibrated against NBS Station WWV time signals. Densities were determined using 25-ml Reischauer pycnometers which had been calibrated with freshly distilled water. Appropriate buoyancy corrections were applied prior to the calculation of densities or compositions. Refractive indices were measured with a Spencer-Abbe Model 2214 refractometer. The temperature was controlled within 0.02° C with a Sargent S-84815 thermostatic water bath assembly. The bath thermometer was compared against a NBS-calibrated thermometer.

All measurements were made in duplicate, and corre-

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Table I. Properties of EC–NMA, DMSO–EC, and DMSO–NMA Mixtures at 40° C

First component							
Wt %	Mol %	ϵ	η	ρ	n_D	$\Delta\epsilon$	ΔV^E
			EC-NMA Mixtures				
0.00	0.00	164.5[a]	3.012[b]	0.9415[c]	1.4257	0.0	0.00
8.86	7.47	149.6	2.732	0.9668	1.4252	−10.0	−0.05
20.76	17.86	132.8	2.456	1.0027	1.4247	−20.0	−0.10
32.34	28.41	120.1	2.246	1.0398	1.4240	−25.4	−0.12
42.65	38.17	111.5	2.099	1.0750	1.4233	−27.1	−0.12
52.64	47.99	104.1	1.984	1.1116	1.4228	−27.4	−0.13
61.73	57.24	98.6	1.903	1.1467	1.4221	−25.9	−0.11
71.22	67.26	94.2	1.845	1.1858	1.4215	−22.6	−0.10
80.19	77.07	91.0	1.814	1.2254	1.4209	−18.1	−0.09
88.88	86.90	89.5	1.824	1.2659	1.4198	−11.4	−0.04
97.36	96.84	89.4	1.893	1.3096	1.4194	−3.2	−0.09
100.00	100.00	89.8	1.930	1.3218	1.4195	0.0	0.00
			DMSO-EC Mixtures				
0.00	0.00	89.8[d]	1.930[e]	1.3218[f]	1.4195[g]	0.0	0.00
6.45	7.21	85.5	1.862	1.3017	1.4223	−0.8	0.07
15.78	17.44	79.9	1.786	1.2738	1.4272	−1.5	0.16
26.12	28.49	74.2	1.709	1.2444	1.4323	−2.0	0.25
34.24	36.98	70.0	1.656	1.2227	1.4366	−2.2	0.29
43.94	46.90	65.6	1.611	1.1982	1.4415	−2.1	0.32
53.72	56.68	61.5	1.571	1.1749	1.4461	−1.8	0.31
64.76	67.44	57.0	1.538	1.1499	1.4520	−1.5	0.30
77.68	79.69	52.5	1.515	1.1227	1.4587	−0.7	0.23
86.48	87.82	49.4	1.510	1.1053	1.4631	−0.3	0.15
96.98	97.32	45.7	1.511	1.0859	1.4690	0.0	0.03
100.00	100.00	44.6	1.513	1.0804	1.4706	0.0	0.00
			DMSO-NMA Mixtures				
0.00	0.00	164.5	3.012	0.9415	1.4257	0.0	0.00
7.90	7.43	141.3	2.725	0.9517	1.4285	−14.8	−0.04
18.69	17.70	118.1	2.420	0.9658	1.4329	−26.2	−0.09
28.94	27.59	101.5	2.198	0.9794	1.4371	−31.6	−0.12
39.59	38.01	88.0	2.010	0.9938	1.4419	−32.9	−0.14
49.30	47.64	78.0	1.888	1.0072	1.4460	−31.5	−0.15
58.99	57.37	69.3	1.780	1.0203	1.4507	−28.5	−0.12
68.70	67.25	62.2	1.696	1.0343	1.4550	−23.5	−0.11
77.64	76.47	56.4	1.626	1.0477	1.4596	−17.9	−0.13
88.06	87.34	50.5	1.567	1.0622	1.4646	−10.3	−0.03
97.40	97.23	46.0	1.522	1.0764	1.4691	−2.2	−0.01
100.00	100.00	44.6[h]	1.513[i]	1.0804[j]	1.4706	0.0	0.00

[a] ϵ = 164.7 (2), ϵ = 165.1 (*3*). [b] η = 3.020 (*15*), η = 3.04 (7). [c] ρ = 0.9415 (7). [d] ϵ = 89.6 (*10*), ϵ = 89.1 (*14*). [e] η = 1.850 (*10*). [f] ρ = 1.3208 (*10*). [g] n_D = 1.4199 (*10*). [h] ϵ = 45.5 (*12*). [i] η = 1.516 (*13*). [j] ρ = 1.0806 (*13*).

sponding values agreed consistently within the expected limits of 0.2% for dielectric constants and viscosities and 0.02% for densities and refractive indices. Mean values are reported for the experimental data.

Fusion point data were obtained by the Addison-Sheldon method (*1*). Normally the determination of the temperature of complete fusion for a mixture was reproducible easily within 0.1° C on consecutive trials.

RESULTS AND DISCUSSION

The experimental and calculated results for the three binary systems at 40° C are summarized in Table I. The footnotes to the sections of this table provide some comparison data for the physical properties of the pure solvents which generally agree closely with our results.

The volumetric behavior for each system is shown in terms of molar excess volumes, $\Delta V^E = V - (X_iV_i + X_jV_j)$. The very slight deviations from ideal molar volumes are expansive ($\leq$0.4%) for the DMSO-EC system whereas these are contractive ($\leq$0.2%) for the EC-NMA and DMSO-NMA systems. The uncertainty associated with each ΔV^E value is estimated to be $\pm$0.04 cc/mol which is of the same magnitude as several of the ΔV^E values.

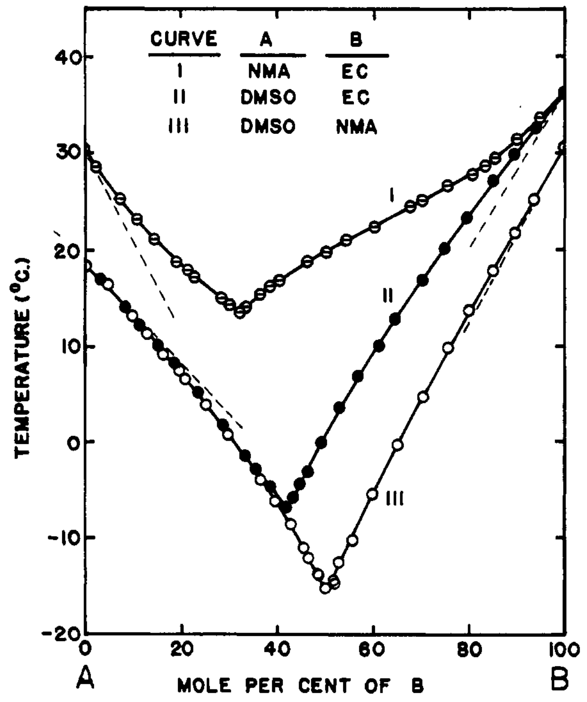

Figure 1. Fusion point curves for some binary systems. Dashed lines illustrate theoretical limiting slopes

The dielectric constant behavior for each system is reflected in terms of a deviation function, $\Delta\epsilon = \epsilon - (\phi_i\epsilon_i + \phi_j\epsilon_j)$, representing the deviation of an experimental value from that related to an ideal volume mixture (*5, 9*). The ϕ_i and ϕ_j are volume fractions of the components based on densities of the pure liquids. The tabulated $\Delta\epsilon$ values reveal that all deviations are negative and are very much greater for the two NMA-containing systems. The large deviations for the EC-NMA and DMSO-NMA systems may be indicative of changes in the nature and extent of alignment of dipoles with changing composition; however, these deviations are considerably less than those reported for *N*-methylpropionamide-water mixtures (*9*).

The viscosity as a function of composition passes through a slight minimum for each of the EC-containing systems whereas the viscosity varies monotonically and nonlinearly with composition for NMA-DMSO mixtures.

For each system the molar refraction is, for practical purposes, a linear function of mole fraction composition. Calculated values,

$$\mathrm{MR} = [(n_D^2 - 1)/(n_D^2 + 2)][(X_iM_i + X_jM_j)/\rho]$$

show a maximum difference of only $\pm$0.04 cc/mol: or $\pm$0.2%, from values for ideal mixtures:

$$\mathrm{MR} = X_i(\mathrm{MR})_i + X_j(\mathrm{MR})_j$$

The fusion (or freezing) point curves for the three systems are shown in Figure 1. Essentially ideal behavior is displayed by the freezing point depression of DMSO by NMA and EC. In these cases the limiting slopes of the curves in Figure 1 are almost identical with the theoretical slope calculated from the expression, $dT/d(\ln X_j) = RT_f^2/\Delta H_f$. In contrast, the freezing point depressions of NMA by DMSO and EC, and of EC by NMA and DMSO, show considerable deviations from theoretical behavior. Experimental values for the freezing points of the pure solvents along with literature values for their cryoscopic constants

Table II. Constants for Pure Solvents

Solvent	Exptl fp, °C	K_f, deg kg/mol	ΔH_f, kcal/mol[a]
NMA	30.6	6.65 (*3*)	2.02
DMSO	18.5	4.07 (*6*)	3.24
EC	36.5	7.03 (*8*)	2.39

[a] $\Delta H_f = \mathrm{MR}\ T_f^2/10^3 K_f$.

and molar enthalpies of fusion, used in calculating the limiting slopes of the freezing point curves, are summarized in Table II.

NOMENCLATURE

NMA = N-methylacetamide
DMSO = dimethyl sulfoxide
EC = ethylene carbonate
ϵ = dielectric constant
η = viscosity, cP
ρ = density, g/cc
n_D = refractive index (sodium D line)
V = molar volume, cc/mol
ΔV^E = molar excess volume, cc/mol
ϕ = volume fraction
X = mole fraction
M = molecular weight, g/mol
ΔH_f = molar enthalpy of fusion, kcal/mol
R = molar gas constant, kcal/(mol deg)
MR = molar refraction, cc/mol
T = temperature, °K
T_f = freezing point, °K
K_f = cryoscopic constant, deg kg/mol

Subscripts

i, j = generalized components

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Density and Viscosity of Aqueous Solutions of Methanol and Acetone from the Freezing Point to 10°C

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The viscosities and densities of aqueous solutions of methanol and acetone are presented. Compositions studied ranged from 50–100 wt % for methanol solutions and 60–100 wt % for acetone solutions. Data were taken from the freezing points of the solutions up to +10° C at 10-degree intervals. A Cannon-Ubbelohde viscometer and a glass cell pycnometer were used to make the experimental measurements. The estimated precision of the measurements was ±1.9% for viscosity and 0.0002 gram/ml for density. No data have been previously reported for these systems below room temperature.

Growing industrial interest in cryogenic processing has greatly increased the need for reliable physical property data of fluid systems at low temperatures. Associated with such cryogenic processes are related processes which are carried out at moderately low temperatures. These moderately low temperatures can often be achieved more economically by refrigeration without the use of cryogens.

To design systems for achieving these moderately low temperatures, transport properties of fluids to be used as heat transfer media must be known. A search of the literature showed that these types of data are virtually nonexistent. Therefore, this study was undertaken to obtain reliable viscosity and density data for aqueous solutions of methanol and acetone from the freezing point to 10° C.

PREVIOUS WORK

Howard and McAllister (*3*) report the viscosity of acetone–water over the entire composition range from 20° C to the boiling point. Thomas and McAllister (*8*) report the densities of the same compositions and temperatures. Kurtz et al. (*4*) report the densities over the entire composition range at 20° and 25° C. These three articles represent the bulk of all previous work done on the acetone–water

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