Subscript

1	cyclohexane
2	cyclohexanone

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Some Physicochemical Properties of the Binary Mixtures Heptane–Propanone and Heptane–Ethyl Acetate

F. Vanden Kerchove* and M. De Vijlder
Rijksuniversiteit Gent, Laboratorium voor Fysische Scheikunde, Krijgslaan 271, B-9000 Gent, Belgium

The density, viscosity, dielectric constant, and electric conductivity of binary mixtures of propanone or ethyl acetate with heptane were measured at 22.5 °C. The experimental results are expressed as functions of the mole fractions. The excess volumes are given. The equations of Mc Allister and Heric for the viscosity of binary systems are applied. Different relationships, expressing the dielectric constants of mixtures, are tested. A new equation is proposed to calculate the electric conductivity from the conductivities of both components. The results agree with the results for mixtures containing ethyl acetate. There are deviations for the system propanone–heptane.

In the framework of a systematic study on the electrokinetic behavior of liquids and liquid mixtures of very low conductivity, it was necessary to know the values of certain physicochemical properties of binary mixtures of heptane with propanone (system A) or with ethyl acetate (system B), i.e., the density, viscosity, static dielectric constant, and electric conductivity.

In this paper, experimental results are presented concerning these properties, on which hitherto no literature data were available.

In view of their application in the electrokinetic study, the properties are correlated by simple power series of the molar fraction of the polar component. The validity of existing equations for the viscosity and the dielectric properties is tested.

In order to explain the electric conductivity of these mixtures a new relation is proposed and checked.

Experimental Section

Materials. All liquids were GR products (Merck). Before use they were distilled in an all-glass multiple-plate still. The purity of the constant boiling point fraction was checked by gas chromatography. All mixtures were prepared by weighing.

Density Measurements. The density ρ was determined by means of a pycnometer of about 10 cm^3 volume. Each reported density is the mean value of three sample weighings. No correction to vacuum was applied. The solutions were not degassed. To prevent loss of weight by evaporation, the pycnometer and the mixture were thermostated separately at 22.5 °C. The pycnometer was weighed immediately after filling.

Viscosity Measurements. The viscosity η was determined by means of an Ostwald viscometer, placed in a thermostat at 22.5 °C. The time of effluence of the apparatus always exceeded 100 s. The measurement was repeated until three equal time values were obtained.

Measurement of the Static Dielectric Constant. The dielectric constant ϵ of the liquids was determined by means of a WTW-Dekameter DK03. The value of ϵ is deduced from the measurement of the cell capacitance at 1.8 MHz. The cell was thermostated at 22.5 °C by a circulating water jacket.

Measurement of Electric Conductivity. The resistance of all mixtures was measured in a stainless steel cell, described by Klinkenberg (*7*). The cell constant (7.19 × 10^{-3} cm^{-1}) was determined by means of a 10^{-3} M KCl solution. Because of the wide range of conductivities (from 10^{-7} to 10^{-17} Ω^{-1} cm^{-1}), different measuring devices were used.

Resistances less than 10^6 Ω were determined with a Philips Measuring Bridge GM 4249. For higher resistances (up to 10^{10} Ω) a Keithley Electrometer 610 A was used. To determine resistances above 10^{10} Ω, five external dc voltages (100, 200, 300, 400, and 500 V) were subsequently applied to the cell and the resulting currents were measured. From the slope of the resulting linear current–voltage plot, the resistance was deduced. As the conductivity cell could not be placed in a thermostated water bath, the mixture was placed preliminarily in the bath and then poured into the cell, while keeping the room temperature as near to 22.5 °C as possible.

Results

Density. The density data are listed in Table I, which also contains the values of the molar volume (V_m) of each sample:

$$V_m = \frac{x_1M_1 + x_2M_2}{\rho} \tag{1}$$

The excess volume V_E is the difference between the actual molar volume and the molar volume of an ideal mixture:

$$V_E = V_m - (x_1V_1 + x_2V_2) \tag{2}$$

The excess volumes of both systems are plotted in Figure 1 as a function of x_1. They can be fitted to

$$V_E = kx_1x_2 \tag{3}$$

This equation is represented by the full line in Figure 1, calculated with a value of k = 4.4.

Table I. Density and Dielectric Constant of Binary Systems at 22.5 °C

x_1	ρ (g cm^{-3})	V_m (cm^3 mol^{-1})	ϵ_{expti}	ϵ_{calcd} Eq 12	Eq 13	Eq 14
System A Propanone (1)-Heptane (2)						
0.0000	0.6808	147.19	1.92	1.93	1.93	1.93
0.0903	0.6846	140.82	2.45	2.63	2.65	2.59
0.1832	0.6883	134.38	3.09	3.54	3.58	3.40
0.2402	0.6918	130.23	3.56	4.18	4.23	3.97
0.3204	0.6964	124.52	4.33	5.19	5.27	4.85
0.3687	0.7001	120.96	4.83	5.86	5.95	5.43
0.4332	0.7040	116.42	5.64	6.82	6.94	6.29
0.4791	0.7081	113.02	6.28	7.57	7.71	6.95
0.5431	0.7144	108.24	7.29	8.70	8.85	7.97
0.5839	0.7183	105.26	8.21	9.48	9.64	8.68
0.6392	0.7241	101.20	9.43	10.61	10.77	9.74
0.7283	0.7361	94.45	11.54	12.64	12.81	11.70
0.7704	0.7428	91.21	12.69	13.71	13.87	12.76
0.8059	0.7481	88.56	13.71	14.67	14.83	13.74
0.8175	0.7491	87.80	14.07	15.00	15.15	14.08
0.8841	0.7610	82.74	16.35	17.00	17.12	16.24
0.9073	0.7658	80.94	17.21	17.76	17.87	17.09
0.9393	0.7730	78.44	18.55	18.87	18.94	18.36
0.9625	0.7811	76.38	19.51	19.71	19.75	19.36
1.0000	0.7899	73.53	21.15	21.15	21.15	21.15
System B. Ethyl Acetate (1)-Heptane (2)						
0.0000	0.6812	147.10	1.92	1.93	1.93	1.93
0.1149	0.6959	142.00	2.21	2.19	2.20	2.16
0.1188	0.6966	141.80	2.22	2.20	2.21	2.17
0.1620	0.7038	139.61	2.33	2.32	2.32	2.27
0.2226	0.7117	137.02	2.50	2.48	2.49	2.42
0.2761	0.7204	134.48	2.65	2.64	2.65	2.57
0.3401	0.7312	131.43	2.85	2.85	2.86	2.76
0.3959	0.7410	128.77	3.04	3.04	3.05	2.94
0.4069	0.7430	128.25	3.08	3.08	3.09	2.97
0.4741	0.7558	125.00	3.31	3.33	3.34	3.21
0.5239	0.7661	122.53	3.50	3.53	3.54	3.40
0.5981	0.7829	118.76	3.80	3.84	3.86	3.70
0.6286	0.7901	117.21	3.93	3.98	4.00	3.83
0.6607	0.7988	115.44	4.09	4.13	4.15	3.98
0.7242	0.8152	112.18	4.42	4.44	4.46	4.29
0.7685	0.8261	110.04	4.62	4.68	4.69	4.52
0.7795	0.8290	109.51	4.68	4.73	4.75	4.59
0.8640	0.8549	104.99	5.16	5.21	5.22	5.09
0.9108	0.8685	102.70	5.45	5.49	5.50	5.40
0.9599	0.8850	100.11	5.77	5.81	5.81	5.76
1.0000	0.8994	97.97	6.08	6.08	6.08	6.08

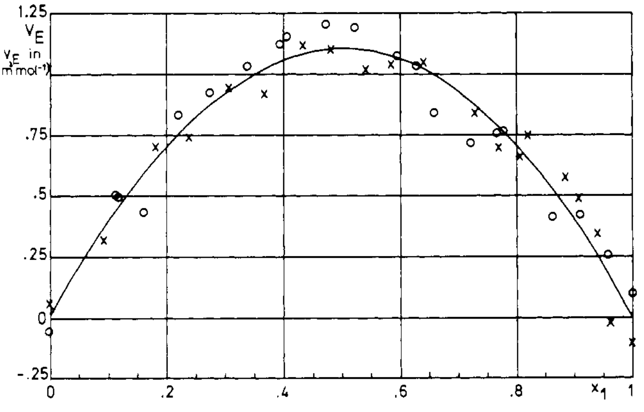

Figure 1. Excess volumes as a function of mole fraction composition: X, system A, propanone-heptane mixtures; O, system B, ethyl acetate-heptane mixtures; full line, calculated with $V_E = 4.4\, x_1x_2$.

The proportionality of V_E to x_1x_2 is one of the requirements of a regular solution (*10*) and corresponds to a quadratic equation for V_m:

$$V_m = A_V + B_Vx_1 + C_Vx_1^2 \qquad (4)$$

Table II. Parameters for the Molar Volume Expression $V_m = A_V + B_Vx_1 + C_Vx_1^2$

Parameter	Value (in cm^3 mol^{-1}) System A propanone-heptane	System B ethyl acetate-heptane
A_V	147.14	147.16
B_V	−69.17	−44.86
C_V	−4.33	−4.42
V_1	73.64	97.88

Table III. Viscosity of Binary Systems at 22.5 °C

System A propanone (1)-heptane (2) x_1	η (in cP)	System B ethyl acetate (1)-heptane (2) x_1	η (in cP)
0.0000	0.395	0	0.397
0.0795	0.385	0.0713	0.391
0.1252	0.377	0.1748	0.385
0.1699	0.370	0.2448	0.382
0.2532	0.362	0.3468	0.382
0.3008	0.358	0.4832	0.383
0.3956	0.351	0.4946	0.381
0.4536	0.347	0.5009	0.382
0.5061	0.342	0.5867	0.387
0.6193	0.333	0.6508	0.392
0.6981	0.328	0.7653	0.403
0.7504	0.321	0.8485	0.413
0.8116	0.316	0.8885	0.420
0.8666	0.314	1.0000	0.437
0.9144	0.309		
0.9678	0.311		
1.0000	0.311		

where $A_V = V_2$, $B_V = k + V_1 - V_2$, and $C_V = -k$. The values of A_V, B_V, and C_V and hence of V_1, V_2, and k were determined by quadratic regression. The values of the parameters are listed in Table II. The standard error of estimate of the densities was 0.0006 in system A and 0.0007 in system B.

Viscosity. The data on the viscosity of both systems are listed in Table III. We correlated $\ln(\eta V_m)$ as a cubic function of x_1

$$\ln(\eta V_m) = A_\eta + B_\eta x_1 + C_\eta x_1^2 + D_\eta x_1^3 \qquad (5)$$

The values of the coefficients were calculated by regression and are listed in Table IV. The standard error of estimate was 5.9 × 10^{-3} for system A and 3.3 × 10^{-3} for system B.

Dielectric Constant. Column 4 of Table I contains the experimental values of ϵ. These values were correlated by a cubic equation

$$\epsilon = A_\epsilon + B_\epsilon x_1 + C_\epsilon x_1^2 + D_\epsilon x_1^3 \qquad (6)$$

The coefficients, obtained by regression, are listed in Table V, together with the standard error of estimate (SEE).

Electric Conductivity. The measured values of κ are plotted in Figure 2 as a function of x_1

Discussion

Equation 5, correlating $\ln(\eta V_m)$ with x_1, is of the same functional form as the equations of Mc Allister (*8*) and of Heric (*6*). Both approaches are based on Eyring's kinetic model of viscosity. Mc Allister used a three-body model and considered four possible processes: (a) a molecule of component 1 moving between two identical molecules (kinematic viscosity ν_1), (b) a molecule of component 2 moving between two identical molecules (ν_2), (c) a three-body interaction between two molecules of component 1 and one molecule of component 2 (ν_{12}), and (d) an interaction of one molecule of component 1 and two mole-

Table IV. Correlation of Viscosity Data

	System A propanone–heptane	System B ethyl acetate–heptane
A_η	4.059	4.069
B_η	−0.809	−0.537
C_η	−0.006	0.223
D_η	−0.119	0.010
η_1	0.309 (in cP)	0.441 (in cP)
η_2	0.394 (in cP)	0.397 (in cP)
ν_{12}	0.467 (in cSt)	0.478 (in cSt)
ν_{21}	0.513 (in cSt)	0.508 (in cSt)
β	0.184	−0.239
β'	0.060	−0.005

cules of component 2 (ν_{21}). This model leads to a cubic equation for the kinematic viscosity ν of a binary mixture

$$\ln\left[(M_1x_1 + M_2x_2)\nu\right] = x_1^3\ln(M_1\nu_1) + 3x_1^2x_2\ln\left[\left(\frac{2M_1}{3}+\frac{M_2}{3}\right)\nu_{12}\right] + 3x_1x_2^2\ln\left[\left(\frac{M_1}{3}+\frac{2M_2}{3}\right)\nu_{21}\right] + x_2^3\ln(M_2\nu_2) \quad (7)$$

Conversion of ν, ν_1, and ν_2 into η/ρ, η_1/ρ_1, and η_2/ρ_2 and elimination of all ρ's by means of eq 1 leads to eq 5, where the coefficients stand for

$$A_\eta = \ln(\eta_2V_2) \quad (8a)$$

$$B_\eta = 3\ln\left[\left(\frac{M_1}{3}+\frac{2M_2}{3}\right)\nu_{21}\right] - 3A_\eta \quad (8b)$$

$$C_\eta = 3\ln\left[\left(\frac{2M_1}{3}+\frac{M_2}{3}\right)\nu_{12}\right] - 2B_\eta - 3A_\eta \quad (8c)$$

$$D_\eta = \ln(\eta_1V_1) - A_\eta - B_\eta - C_\eta \quad (8d)$$

Heric, on the other hand, modified an existing relationship in order to obtain a better fit to empirical results. Therefore he introduced the asymmetry term $x_1x_2\beta'(x_1 - x_2)$:

$$\ln\left[(M_1x_1 + M_2x_2)\nu\right] = x_1\ln(M_1\nu_1) + x_2\ln(M_2\nu_2) + \beta x_1x_2 + \beta'(x_1 - x_2)x_1x_2 \quad (9)$$

The last two terms of this equation describe the deviation from ideality. By conversion of kinematic viscosities into dynamic ones and elimination of the densities, eq 5 is again obtained, but now the coefficients stand for

$$A_\eta = \ln(\eta_2V_2) \quad (10a)$$

$$B_\eta = \ln(\eta_1V_1) - \ln(\eta_2V_2) + \beta - \beta' \quad (10b)$$

$$C_\eta = -\beta + 3\beta' \quad (10c)$$

$$D_\eta = -2\beta' \quad (10d)$$

The values of η_1, η_2, ν_{12}, and ν_{21}, calculated from eq 8a–d, and β and β', calculated from eq 10c–d, are reported in Table IV. For the mixtures containing propanone, β appears to be positive; i.e., the viscosity is higher than that corresponding to ideal mixtures, whereas for system B, the viscosity is lower than for ideal mixtures. For both systems, however, β', the correction coefficient introduced by Heric, appears to be of minor importance. The minimum of η at $x_1 \approx 0.5$ in system B may indicate some association in pure ethyl acetate, which is weakened by adding heptane. In the other system, however, there is a monotonic increase of η. The positive values of both excess volumes are also an indication of the dissociation of associated molecules in the polar liquids by dilution with heptane.

There has been done a lot of theoretical work on dielectric liquid mixtures, especially on those containing a polar component and a nonpolar one. The interest in the dielectric properties is greatly directed to the knowledge of the permanent dipole moment μ of the polar component. Different formulas are known, relating the dielectric constant of a mixture to the polarizability α and the dipole moment of the pure components. They all consider the environment of the molecule to be a continuum with the macroscopic properties of the dielectric, while the dipole is situated in the center of a spherical cavity. The quantities α and μ are considered to be intrinsic parameters of the molecules, independent of the surrounding continuum. The oldest of these equations,

Table V. Parameters for $\epsilon = A_\epsilon + B_\epsilon x_1 + C_\epsilon x_1^2 + D_\epsilon x_1^3$

	System A propanone–heptane	System B ethyl acetate–heptane
A_ϵ	1.91	1.91
B_ϵ	5.87	2.51
C_ϵ	1.08	0.29
D_ϵ	12.24	1.35
SEE	0.06	0.008
RMSD (eq 12)	0.88	0.03
RMSD (eq 13)	0.99	0.04
RMSD (eq 14)	0.37	0.08

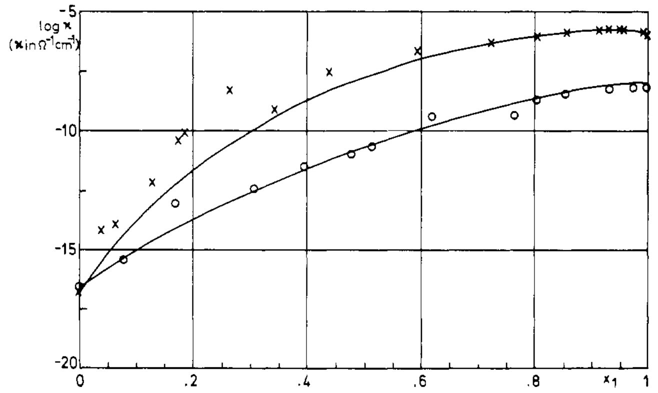

Figure 2. Electric conductivity as a function of mole fraction composition: ×, system A, propanone–heptane mixtures; O, system B, ethyl acetate–heptane mixtures; full lines, calculated from eq 21.

$$\frac{3(\epsilon - 1)}{4\pi(\epsilon + 2)} = \frac{N_1\mu_1^2}{3kT} + N_1\alpha_1 + N_2\alpha_2 \quad (11)$$

formulated by Debye, is no longer used for binary mixtures because it is only valid for very low concentrations of the polar component. By accounting for the contribution from the so-called reaction field γ of the polar molecule to the internal field, Onsager (*9*) deduced the relationship

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{12\pi\epsilon} = \frac{N_1\mu_1}{3kT(1 - \gamma(\alpha_1/a_1^3))^2} + \frac{N_1\alpha_1}{1 - \gamma(\alpha_1/a_1^3)} + \frac{N_2\alpha_2}{1 - \gamma(\alpha_2/a_2^3)} \quad (12)$$

where $\gamma = 2(\epsilon - 1)/2\epsilon + 1$. Barriol and Weisbecker (*1*) pointed out that the reaction field factor $\gamma(\alpha_j/a_j^3)$ should be the same for both components in order to make eq 12 compatible at high frequencies with the Clausius–Mossotti equation. Hence eq 12 was modified into

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{12\pi\epsilon} = \frac{N_1\mu_1}{3kT(1 - \gamma f)^2} + \frac{N_1\alpha_1}{1 - \gamma f} + \frac{N_2\alpha_2}{1 - \gamma f} \quad (13)$$

where $f = 4\pi/3(N_1\alpha_1 + N_2\alpha_2)$. Recently Grosse and Greffe (*5*) developed a still more complex formula

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{12\pi\epsilon} = \frac{N_1\mu_1\eta_2'}{3kT(1 - f_2'\gamma(\alpha_1/a_1^3))^2} + \frac{N_1\alpha_1\eta_2'}{1 - f_2'\gamma(\alpha_1/a_1^3)} + \frac{N_2\alpha_2\eta_1'}{1 - f_1'\gamma(\alpha_2/a_2^3)} \quad (14)$$

in which η' and f' themselves are functions of ϵ:

$$\eta_j' = \frac{2\epsilon + 1}{1 - z_j(\epsilon - \epsilon_j)} \quad (15a)$$

$$f_j' = \frac{1 - \dfrac{z_j(\epsilon_j + 2)(\epsilon - \epsilon_j)}{2(\epsilon_j - 1)(\epsilon - 1)}}{1 - \dfrac{z_j(\epsilon - \epsilon_j)}{2\epsilon + 1}} \quad (15b)$$

and

$$z_j = \frac{8\pi(\epsilon_j + 2)N_j\alpha_j}{9\epsilon_j} \quad (15c)$$

The derivation of this formula is based upon a double-layer model; each molecule is surrounded by a layer with such an excess of molecules of the other component that a minimum volume exists with the same composition and properties as the macroscopic ones.

For the calculation of ϵ of a given mixture, one has to substitute α_j, a_j^3, and N_j in eq 12, 13, and 14 by the following equations:

$$\alpha_j = \frac{3}{4\pi N_{j,0}} \frac{n_j^2 - 1}{n_j^2 + 2} \text{ (Lorenz-Lorentz equation)} \quad (16a)$$

$$N_j = \frac{x_j N_A}{V_m} \quad (16b)$$

$$a_j^3 = \frac{3V_j}{4\pi N_A} \quad (16c)$$

The values of μ (3.12 D for propanone and 1.75 D for ethyl acetate) were calculated from the dielectric constant of the pure component. The values of the refraction index were taken from the literature (*3*): $n_1 = 1.352$ for propanone, $n_1 = 1.372$ for ethyl acetate, and $n_2 = 1.388$. The values of ϵ, computed according to eq 12, 13, and 14, are listed in Table I. The agreement to the measured values is best for the mixtures containing ethyl acetate: the equations of Onsager and Barriol-Weisbecker give a small but systematic deviation with too high results, the equation of Grosse and Greffe deviates in the opposite direction.

For the mixtures with propanone, the deviations are more important. The results of all three equations are much too high; the deviations are the smallest for eq 14 but even these amount to more than 10% for x_1 in the range from 0.20 to 0.50.

The root-mean-square deviation (RMSD) of the values of ϵ, computed from eq 12, 13, and 14, are listed in Table V. It is obviously impossible to decide which of the three equations describes best the dielectric behavior of binary mixtures. Equations 16b and 16c assume the volume of the mixture to be equal to the volume of an ideal mixture. Although this is not correct, the maximum volume deviation of 1%, which is typical of many polar-nonpolar mixtures, is clearly insufficient to make agreement significantly better. The use of the actual volume reduces the calculated values of ϵ by no more than 1%. The discrepancies might be explained by taking into account that the shape of the molecules is not spherical as assumed in eq 12, 13, and 14. Böttcher (*2*), considering the influence of the ellipsoidal shape of the cavities, refers, e.g., to a lowering of μ of about 10% for pure propanone when assuming an ellipsoidal cavity. However, the influence of the shape of nonspherical molecules upon ϵ of mixtures is not yet elucidated.

The electric conductivity of liquids may be attributed to the dissociation of weak electrolyte solutes, often present as impurities in solution. The dissociation equilibrium of the electrolyte may be described by Bjerrum's theory of ion pair formation. Fuoss (*4*) finds for the dissociation constant K of a symmetrical electrolyte ($c_+ = c_-$)

$$\frac{1}{K} = \frac{4\pi N_A a^3 e^b}{3000} = \frac{c}{c_+^2} \quad (17)$$

where

$$b = \frac{|z_+z_-|e^2}{a\epsilon kT}$$

and a is the distance of closest approach of the centers of the two ions forming the ion pair. The concentrations c_1 or c_2 of the undissociated electrolyte solutes may be obtained from the conductivity κ_1 or κ_2 of the pure components:

$$c = \frac{\kappa^2}{\Lambda^2}\frac{1}{K} = \frac{\kappa^2}{\Lambda^2}\frac{4\pi N_A a^3 e^b}{3000} \quad (18)$$

Λ stands for the sum of the equivalent conductances of the oppositely charged ions. By putting a reasonable value of Λ into eq 18, it appears that concentrations in the range from 10^{-9} to 10^{-6} mol L^{-1} might account for the observed conductivities. For binary mixtures

$$c = \frac{x_1c_1V_1 + x_2c_2V_2}{V_m} \quad (19)$$

Combining eq 18 and 19 with the value of κ_1 and κ_2, the equation for binary mixtures becomes

$$\frac{a^3\kappa^2V_me^b}{\Lambda^2} = \frac{a_1^3x_1\kappa_1^2V_1e^{b_1}}{\Lambda_1^2} + \frac{a_2^3x_2\kappa_2^2V_2e^{b_2}}{\Lambda_2^2} \quad (20)$$

Neglecting the small differences between Λ, Λ_1, and Λ_2 (as compared with the large changes of κ and e^b) and assuming a constant value of a, eq 20 reduces to

$$\kappa = \sqrt{\frac{x_1\kappa_1^2V_1e^{b_1} + x_2\kappa_2^2V_2e^{b_2}}{V_me^b}} \quad (21)$$

Although the identity of the proposed impurities remains hitherto unknown, we have obtained an equation containing only one adjustable parameter, i.e., the factor $a/|z_+z_-|$ in the denominator of the exponents. The full lines in Figure 2 are calculated according to eq 21 with a value of $a/|z_+z_-| = 5 \times 10^{-8}$ cm for system A and 4.7×10^{-8} cm for system B. The agreement is remarkable for the latter system. For the former one, however, there are systematic deviations in the high resistance ranges. These deviations might be remedied for by assuming different impurity species in propanone and heptane and hence different values of a. Nevertheless, the plot lends extra support to the hypothesis that impurities may account for the observed conductivities. It can be concluded that mixtures of propanone or ethyl acetate with heptane are suitable systems for electrokinetic measurements, as they cover a wide range of conductivities and dielectric constants, while the densities and the viscosities of the mixtures may be expressed in very simple equations.

Glossary

a	distance of closest approach
a_1, a_2	radius of the spherical cavity in the pure components
A_V, B_V, C_V	coefficients of the molar volume regression line
A_η, B_η, C_η, D_η	coefficients of the viscosity regression line
A_ϵ, B_ϵ, C_ϵ, D_ϵ	coefficients of the dielectric constant regression line
b	parameter in the Fuoss equation for the mixture

b_1, b_2	parameter in the Fuoss equation for the pure components
c	concentration of the undissociated electrolyte solute
c_+, c_-	concentration of the electrolyte ions
e	4.803×10^{-10} esu
f_1', f_2'	correction factors in the equation of Grosse and Greffe
M_1, M_2	molar masses
N_A	6.022×10^{23} mol^{-1}
N_1, N_2	number of molecules of each component in 1 cm^3 of the mixture
n_1, n_2	refraction index of the pure components
T	absolute temperature
V_E	excess volume of the mixture
V_m	molar volume of the mixture
V_1, V_2	molar volume of the pure components
x_1	mole fraction of the polar component
x_2	mole fraction of heptane
z_+, z_-	valency of the electrolyte ions
α	polarizability of the mixture
α_1, α_2	polarizability of the pure components
β, β'	interaction parameters of the equation of Heric
γ	reaction field of the polar molecule
ϵ	dielectric constant of the mixture
ϵ_1, ϵ_2	dielectric constant of the pure components
η	dynamic viscosity (in cP) of the mixture
η_1, η_2	dynamic viscosity (in cP) of the pure components
η_1', η_2'	correction factors in the equation of Grosse and Greffe
κ	conductivity (in Ω^{-1} cm^{-1}) of the mixture
κ_1, κ_2	conductivity (in Ω^{-1} cm^{-1}) of the pure components
μ	dipole moment
ν	kinematic viscosity (in cSt) of the mixture
ν_1, ν_2	kinematic viscosity (in cSt) of the pure components
ν_{12}, ν_{21}	binary parameters of the equation of Mc Allister
ρ	density of the mixture
ρ_1, ρ_2	density of the pure components

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Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 3. The Rare Earth Nitrates

Joseph A. Rard, Loren E. Shiers, David J. Heiser, and Frank H. Spedding*
Ames Laboratory-ERDA and Department of Chemistry, Iowa State University, Ames, Iowa 50011

The osmotic coefficients of the aqueous trinitrates of Sm, Gd, Tb, and Tm have been measured from 0.1–0.2 mol kg^{-1} to saturation, and those of erbium and ytterbium trinitrates have been measured from 0.1 mol kg^{-1} to well into the supersaturated concentration region. In addition, data for La trinitrate have been measured from 0.32 to 1.26 mol kg^{-1}. These osmotic coefficients were fitted to semiempirical least-squares equations, and water activities and mean molal activity coefficients were calculated from these equations. The water activities of these rare earth nitrate solutions are much higher than for the corresponding rare earth chlorides and perchlorates at the same molalities, while the nitrate solution mean molal activity coefficients are much lower. Differences between the activities of the various rare earth salts are discussed in terms of ion–water and ion–ion interactions.

The water activities and activity coefficients of some rare earth chloride (*22*) and perchlorate (*12*) solutions have recently been reported up to saturation at 25 °C. S-Shaped curves result when these properties at constant molality are plotted against the ionic radius of the rare earth ion, from dilute to moderately high concentrations. Although some changes do occur in the shape of these series curves at high concentrations due to the formation of ion-pairs, the shape of each of these series curves over most of the concentration range has been interpreted as being primarily due to changes in the hydration of the rare earth cations. Related series trends also appear in other thermodynamic and transport properties of the rare earth chlorides and perchlorates. The complexes formed in the rare earth chloride and perchlorate solutions are believed to consist predominantly, if not entirely, of outer sphere (i.e., solvent separated) ion-pairs (*2*). Series curves for heats of dilution (*17*), heat capacities (*24*), partial molal volumes (*20*), electrical conductances (*11*), and relative viscosities (*21*) for the rare earth nitrates appear to be S shaped only at relatively low concentrations, while at moderate and high concentrations these properties exhibit more monotone behavior.

Choppin et al. (*2, 3*) have interpreted their spectral and thermodynamic results as indicating that complex formation in dilute rare earth nitrate solutions consists predominantly of outer sphere rare earth nitrate complexes, with a few percent of inner sphere complexes. Ultrasonic absorption results (*5, 15, 16*) suggest that the extent of inner sphere complex formation may be even larger in these solutions. At high concentrations the