Table I. Liquid Properties at 25 °C

liquid	ρ, kg/m^3	$10^6\nu$, m^2/s	$10^3\sigma$, N/m	$c_{\mathrm{sat,CO_2}}$, kmol/(m^3 atm)	$10^9 D_{\mathrm{CO_2}}$, m^2/s	$\nu/D_{\mathrm{CO_2}}$	$10^3\nu\cdot(\rho^3 g/\sigma^3)^{1/4}$
methanol	786.6	0.695	22.2	0.159	8.37	83	3.17
ethanol	785.0	1.400	22.7	0.125	3.88	360	6.28
Aqueous Propanol Solutions							
X = 0.0	997.0	0.893	72.2	0.0346	1.95	458	2.02
0.02	987.2	1.169	41.8	0.0332	1.71	683	3.90
0.05	975.6	1.613	30.5	0.0318	1.43	1128	6.84
0.10	954.2	2.178	26.3	0.0334	1.42	1534	10.14
0.20	916.8	2.790	25.9	0.0429	1.57	1777	12.75
0.50	849.4	2.884	24.9	0.0685	1.93	1494	12.79
1.00	800.0	2.428	23.4	0.0963	2.73	889	10.79
Aqueous Ethylene Glycol Solutions							
X = 0.00	997	0.898	72	0.0346	1.96	458	2.02
0.052	1015	1.30	65	0.0302	1.58	822	3.20
0.12	1036	1.88	61	0.0279	1.22	1540	4.95
0.20	1053	2.75	57.5	0.0270	1.02	2700	7.66

struction of the cell was similar to that of Davidson and Cullen (*5*), except that an improved liquid distributor and takeoff tube were developed. The liquid flow rate was measured by using a rotameter while the gas absorption rate was obtained by using a soap film gas flow meter. The theory used for data reduction was developed in ref *5* and is based on the solution of the steady-state species conservation equation in the liquid film using a parabolic velocity distribution. The effect of solute concentration on diffusion coefficient was assumed to be negligible on the basis of the experimental study of Tang and Himmelblau (*6*).

Density, Viscosity, and Surface Tension. Densities were measured by using a 10-mL adjusted specific gravity bottle, while viscosities were measured by using a Cannon-Fenske (size 50) capillary viscometer. Surface tensions were measured by the ring method using a Du Noüy surface tensiometer. The apparent surface tension registered by the instrument was corrected by using the equation suggested by Zuidema and Walters (*7*).

Results

Table I shows the measured data, together with the dimensionless property groupings ν/D and $\nu(\rho^3 g/\sigma^3)^{1/4}$. Some pertinent comparisons with prior data follow. The solubility in ethanol agrees exactly with the value in the International Critical Tables (*8*). For aqueous ethylene glycol the density, viscosity, and CO_2 solubility agree with the data of Hayduk and Malik (*3*): the CO_2 diffusivity measured for mole fractions of glycol, X, in the range 0–0.2 by using a sphere cell extrapolate smoothly to the values measured in ref *3* by using a stationary capillary cell for X greater than 0.25. For aqueous propanol solutions the density and the viscosity agree well with the data of Mikhail and Kimmel (*4*).

Also given in Table I are the dimensionless groups Schmidt number, Sc = ν/D, for CO_2 and the capillarity-buoyancy number Cb = $\nu(\rho^3 g/\sigma^3)^{1/4}$. Both of these groups are used in the correlation of experimental data for rates of gas absorption into turbulent falling liquid films.

Glossary

c_{sat}	saturation concentration of solute at a gas-phase partial pressure of 1 atm, kmol/(m^3 atm)
D	diffusivity, m^2/s
g	gravitational acceleration, 9.81 m/s^2
X	mole fraction of glycol or propanol
ν	kinematic viscosity, m^2/s
ρ	density, kg/m^3
σ	surface tension, N/m

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Viscosities of Concentrated Aqueous Solutions of Some 1:1, 2:1, and 3:1 Nitrates at 25 °C

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The viscosities and densities of concentrated aqueous solutions of nitrates of K, Na, Cd, Cu(II), Ba, Pb, Sr, Mg, Ni, Zn, and Fe(III) have been measured at 25 °C. The relative viscosities have been fitted to an extended Jones–Dole-type equation.

Introduction

Recently there has been noticeable progress in the theory of the viscosity of electrolyte solutions at concentrations beyond the applicability of the classical Jones–Dole equation (*1a*, *2*). The equation of Breslau and Miller (*3*) is derived from the Einstein–Thomas model of rigid spheres suspended in a continuum. Free volume theory has been applied by Angell and Bressel (*4*), and the most recent example of the use of Eyring's rate process theory is due to Goldsack (*5*). Yet another more recent proposal is that based on the Tammann-Tait-Gibson (TTG) model, which relates the viscosity of the solution to the viscosity of the *water* in the solution (*6*).

We noticed that the data necessary for testing these theories were relatively sparse and that solution chemists have tended to use halide salts as illustrations of their theses (probably because the data for these salts are more abundant and of better quality than others). Nitrates, however, have not been examined in as great detail, particularly those of polyvalent cations. Lack of data is again an evident factor, and it is partly for this reason that we report here viscosities of a number of nitrate solutions at 25 °C.

Experimental Section

It was not the purpose of this work to perform measurements of the highest possible precision. Cannon-Fenske viscometers of usual design were used such that the flow times of water and solution were greater than 100 s. Flow times were determined with stopwatches of 0.1-s precision, the value finally used being an average of three or four observations within 1‰. A 5-mL aliquot of liquid was used for all measurements. The viscometer was placed in a water bath at 25 ± 0.01 °C. The viscometers were rinsed with distilled water and dried with acetone. The interior glass surface was kept clean and unmarked during all measurements, except for $Pb(NO_3)_2$, during which the growth of some white opaqueness was noticed. Although this apparent deposit could not be removed by hot acid, it nevertheless did not affect the final results, as determined by check experiments with a clean viscometer.

Solutions were prepared by weight at round molalities with distilled water. the salts were reagent grade (Baker Analyzed, Fisher Certified, Anachemia or General Chemical Co.): $NaNO_3$, KNO_3, $Zn(NO_3)_2\cdot 6H_2O$, $Ba(NO_3)_2$, $Cd(NO_3)_2\cdot 4H_2O$, $Cu(NO_3)_2\cdot 2.5H_2O$, $Pb(NO_3)_2$, $Sr(NO_3)_2$, $Mg(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $Fe(NO_3)_3\cdot 9H_2O$. All were previously unopened and were used as received. Solutions were kept in stoppered containers to prevent evaporation. Experimental reproducibility was tested for a few solutions by duplicate solution preparation and viscosity measurement. The results were concordant to within 2‰. No consistent attempt was made to proceed to saturation, the criterion being a solution without visible suspended particles. In preparation and use of the $Fe(NO_3)_3$ solutions, the expected hydroxide precipitate did not appear.

The density of each solution was measured with a vibrating-tube-type densimeter (DMA 10, Anton Paar) thermostated at 25 ± 0.02 °C. The instrument was calibrated with air and distilled water, and the manufacturer's stated accuracy for the instrument is $\pm 2.5 \times 10^{-4}$ g mL^{-1}. It has been shown (*7*) that this type of densimeter is subject to error due to the viscosity of the liquid involved, the error increasing with the viscosity. However, even at the highest viscosity reported in this work, the corresponding error is only a fraction of the instrument's accuracy, and no corrections were made to the densities reported herein.

Results and Discussion

The relative viscosity was calculated from eq 1, where d_0 =

$$\eta_r(\text{exptl}) = dt/d_0t_0 \qquad (1)$$

0.9971 g mL^{-1}. Relative viscosities and densities measured in this work are given in Table I. A viscosity–concentration plot for the 2:1 salts appears in Figure 1.

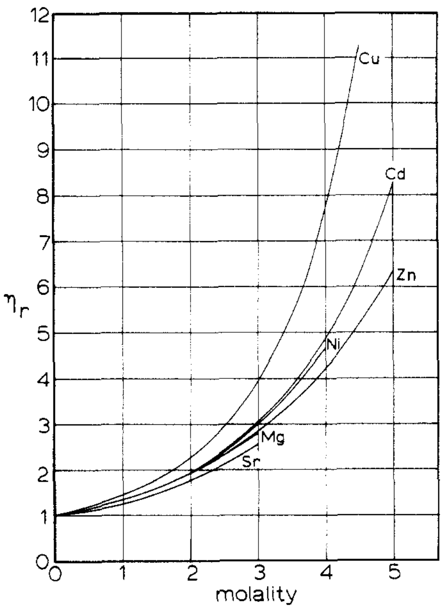

Figure 1. Relative viscosity of solutions of some nitrate salts, $M(NO_3)_2$, at 25 °C. The curves for Ba and Pb overlap that of Sr.

In order to represent these data in a more convenient form, we combined them with whatever other consistent data could be found in the literature (*8*–*10*). These combined data were fitted, to as high a concentration as possible, to eq 2. The

$$\eta_r(\text{calcd}) = 1 + Am^{1/2} + Bm + Dm^2 + Em^3 \qquad (2)$$

parameter A was calculated from the Falkenhagen–Vernon equation (*11a*) by using D_0 = 78.40 (*12*) and η_0 = 0.8903 cP (*13*). The limiting ionic conductances were taken from Harned and Owen (*11b*) or Erdy-Grúz (*1b*). Those not in either of these references were assigned values as follows: Pb^{2+}, 60; Ni^{2+}, 53; Fe^{3+}, 65. Values of B were taken from the compilation of Breslau and Miller (*3*). In order to determine D and E, we plotted the quantity $(\eta_r(\text{exptl}) - 1 - Am^{1/2} - Bm)/m^2$ against m, and the slope and the intercept were determined by least squares at concentrations higher than 1 m. A root-mean-square deviation Δ_{rms} (in parts per thousand) was calculated from eq 3. The upper limit of concentration, m_{max}, was chosen

$$\Delta_{rms} = 1000[(\sum\{\Delta\eta_r/\eta_r(\text{exptl})\}^2)/n]^{0.5} \qquad (3)$$

so as to keep Δ_{rms} to the order of a few parts per thousand. Values of parameters A, B, D, and E appear in Table II for all of the salts except $Zn(NO_3)_2$, for which Δ_{rms} was unacceptably high even at low concentration.

Glossary

A, B, D, E	fitting parameters in eq 2, having units (kg mol^{-1})^x where x = 0.5, 1, 2, and 3, respectively
D_0	dielectric constant of water (unitless)
d_0	density of water (g mL^{-1})
d	density of a solution
m	molality (mol kg^{-1})
n	number of data points
t	flow time for solution (s)
t_0	flow time for water

Greek Letters

η	viscosity of a solution (cP)
η_0	viscosity of water
η_r	relative viscosity = η/η_0 (unitless)
$\Delta\eta_r$	difference between experimental (exptl) and calculated (calcd) values of η_r

Table I. Relative Viscosities and Densities of the Nitrate Solutions at 25 °C, Measured in This Work

m	d	η_r
	$NaNO_3$	
0.5	1.0239	1.024
1.0	1.0500	1.059
1.5	1.0737	1.100
2.0	1.0980	1.152
2.5	1.1201	1.210
3.0	1.1409	1.270
3.5	1.1621	1.340
4.0	1.1820	1.412
4.5	1.2001	1.493
5.0	1.2191	1.580
	KNO_3	
0.50	1.0272	0.982
0.75	1.0416	0.978
1.00	1.0555	0.977
1.25	1.0660	0.976
1.50	1.0823	0.982
1.75	1.0951	0.990
2.00	1.1076	0.997
2.25	1.1197	1.001
2.50	1.1316	1.011
2.75	1.1432	1.019
3.00	1.1544	1.029
	$Zn(NO_3)_2$	
0.1	1.0120	1.030
0.5	1.0713	1.165
1.0	1.1410	1.367
1.5	1.2071	1.626
2.0	1.2687	1.947
2.5	1.3270	2.350
3.0	1.3824	2.853
3.5	1.4346	3.479
4.0	1.4825	4.25
4.5	1.5280	5.23
5.0	1.5707	6.41
	$Cd(NO_3)_2$	
0.1	1.0154	1.034
0.5	1.0908	1.169
1.0	1.1818	1.375
1.5	1.2712	1.644
2.0	1.3574	1.996
2.5	1.4408	2.451
3.0	1.5221	3.044
3.5	1.6012	3.844
4.0	1.6766	4.89
4.5	1.7494	6.29
5.0	1.8210	8.22
	$Cu(NO_3)_2$	
0.1	1.0125	1.035
0.5	1.0739	1.201
1.0	1.1513	1.429
1.5	1.2289	1.779
2.0	1.3053	2.272
2.5	1.3804	2.981
3.0	1.4539	4.00
3.5	1.5262	5.51
4.0	1.5940	7.68
4.5	1.6624	11.09
	$Ba(NO_3)_2$	
0.05	1.0071	1.011
0.10	1.0180	1.019
0.15	1.0280	1.029
0.20	1.0382	1.038
0.25	1.0484	1.049
0.30	1.0583	1.059
0.35	1.0680	1.071
	$Pb(NO_3)_2$	
0.2	1.0526	1.039
0.4	1.1070	1.081
0.6	1.1597	1.132
1.0	1.2599	1.248
1.5	1.3796	1.432
	$Sr(NO_3)_2$	
0.1	1.0147	1.023
0.5	1.0769	1.116
1.0	1.1509	1.278
1.5	1.2197	1.490
2.0	1.2833	1.770
2.5	1.3434	2.130
3.0	1.3991	2.584
	$Mg(NO_3)_2$	
0.5	1.0496	1.167
1.0	1.0988	1.366
1.5	1.1446	1.618
2.0	1.1870	1.932
2.5	1.2266	2.320
3.0	1.2639	2.809
	$Ni(NO_3)_2$	
0.25	1.0281	1.076
0.50	1.0679	1.167
0.75	1.1025	1.268
1.00	1.1365	1.377
1.25	1.1691	1.505
1.50	1.2001	1.645
1.75	1.2329	1.812
2.00	1.2622	1.994
2.50	1.3190	2.432
3.00	1.3749	3.011
3.50	1.4254	3.732
4.00	1.4753	4.70
	$Fe(NO_3)_2$	
0.5	1.0845	1.374
1.0	1.1658	1.953
1.5	1.2406	2.850
2.0	1.3095	4.22
2.5	1.3714	6.27
3.0	1.4292	9.19

Table II. Fitting Parameters for the Equation $\eta_r(\text{calcd}) = 1 + Am^{1/2} + Bm + Dm^2 + Em^3$

salt	10^4A	10^3B	10^3D	10^4E	$m_{\max}$	n	Δ_{rms}(eq 3)
$NaNO_3$	63	40	18.2	−7.53	7.5	22	5.5
KNO_3	50	−53	27.7	−23.0	3	16	3.2
$Cd(NO_3)_2$	170	240	54.0	321	4	12	13
$Cu(NO_3)_2$	170	293	67.3	504	2.5	10	3.3
$Ba(NO_3)_2$	154	128	145	0	0.35	11	1.3
$Pb(NO_3)_2$	160	141	95.0	0	1.5	14	4.5
$Sr(NO_3)_2$	160	173	70.9	149	3	12	3.4
$Mg(NO_3)_2$	172	293	41.8	201	3.7	14	4.6
$Ni(NO_3)_2$	172	292	39.7	283	4	15	4.9
$Fe(NO_3)_3$	307	623	75.6	2065	3	6	5.0

Δ_{rms}	root-mean-square deviation for η_r (eq 3)

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Vapor–Liquid Equilibria in the Dichloromethane–Chlorobromomethane–Dibromomethane System and Its Binaries

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Vapor–liquid equilibria were measured at 760 mmHg for the systems dichloromethane–dibromomethane, dichloromethane–chlorobromomethane, dibromomethane–chlorobromomethane, and dichloromethane–chlorobromomethane–dibromomethane. Boiling points of the systems were correlated by an empirical expression. None of the systems exhibited azeotropic behavior. The activity coefficients in the binary and ternary systems were correlated by the Redlich–Kister and Wilson equations.

Introduction

Halogen derivatives of methane have been studied only in mixtures with aliphatic and aromatic hydrocarbons (*1*, *2*) or with dimethyl sulfoxide (*3*). No data are available on mixtures of derivatives alone. The review by Kehiaian (*4*) also indicates that the number of systems involving halomethanes is very small. Halomethanes have found application in organic synthesis as alkylating agents, in preparation of surface-active agents, and in the manufacture of dyes and pharmaceuticals.

We report here the vapor–liquid equilibrium in the ternary dichloromethane (DCM)–chlorobromomethane (BCM)–dibromomethane (DBM) system and the corresponding binary systems at 760 mmHg. The experimental procedure has already been reported (*5*). The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta T = \pm 0.02$ °C, while the mole fractions in both phases were measured within ±0.001. DCM and DBM were supplied by Bromine Compounds Ltd., Beer-Sheva, and CBM was supplied by Fluka. No significant impurities were detected by gas-chromatographic analysis of these reagents. Except for DBM—which was dried and redistilled—the reagents were used without further purification. Physical properties of the halomethanes are collected in Table I, and they agree with the literature data (*6*). The analyses were carried out by gas chromatography using a Packard-Becker Model 417 apparatus equipped with a thermal conductivitiy detector and an Autolab Minigrator electronic integrator. The column (0.32 × 200 cm) was filled with O.V.17 and maintained at 90 °C; the injection port temperature was 220 °C, and that of the detector 250 °C.

Table I. Physical Properties of Pure Compounds

compd	refractive index at 20 °C	bp, °C
CH_2Cl_2 (1)	1.4230	39.50
	1.4242 (*6*)	39.75 (*6*)
CH_2ClBr (2)	1.4824	68.25
	1.4837 (*6*)	68.11 (*6*)
CH_2Br_2 (3)	1.5400	96.50
	1.5420 (*6*)	96.95 (*6*)

Table II. Vapor-Pressure Constants (*6*)

compd	α_i	β_i	δ_i
CH_2Cl_2 (1)	7.08030	1138.91	231.45
CH_2ClBr (2)	6.86624	1132.30	216.00
CH_2Br_2 (3)	7.06250	1327.80	220.58

Table III. Experimental Vapor-Liquid Equilibria Data for Dichloromethane (1)-Chlorobromomethane (2) at 760 mmHg

temp, °C	x_1	y_1	y_1 calcd[a]
66.44	0.027	0.064	0.064
63.27	0.087	0.186	0.188
62.90	0.101	0.213	0.216
61.78	0.125	0.259	0.258
60.67	0.145	0.291	0.290
59.60	0.173	0.338	0.335
55.80	0.277	0.487	0.475
52.90	0.371	0.588	0.580
51.04	0.434	0.657	0.639
49.20	0.502	0.717	0.695
47.35	0.595	0.787	0.774
45.55	0.652	0.836	0.798
43.98	0.754	0.884	0.875
43.35	0.790	0.902	0.897
41.00	0.917	0.962	0.959

[a] According to Raoult's law.

Results and Discussion

The temperature-composition data at constant pressure (P = 760 mmHg) for the systems under consideration are presented in Tables III–VI. The boiling points of the binary and ternary systems were correlated by eq 1 and 2, where T^0 is

$$T = \sum_{i=1}^{2} T_i^0 x_i + x_1 x_2 \sum_{k=0}^{l} C_k (x_i - x_j)^k \qquad (1)$$

$$T = \sum_{i=1}^{3} T_i^0 x_i + \sum_{i,j=1}^{3} x_i x_j \sum_{k=0}^{l} C_k (x_i - x_j)^k + x_1 x_2 x_3 [A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)] \qquad (2)$$

the boiling point of the pure component expressed in °C, C_k values are the binary constants, and A, B, C, and D are the

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