both temperatures. The pH of the saturated solutions is related to the ratio NH_4-N:P_2O_5 (R) at 0 °C by

$$pH = (-1.27 \pm 0.14) + (24.6 \pm 0.5)R \tag{3}$$

with a correlation coefficient of 0.997 and a prediction standard deviation of 0.04 pH unit, and at 25 °C by

$$pH = (-1.76 \pm 0.17) + (26.7 \pm 0.6)R \tag{4}$$

with a correlation coefficient of 0.996 and a prediction standard deviation of 0.05 pH unit.

Literature Cited

(1) Farr, T. D.; Williard, J. W. *J. Chem. Eng. Data* **1969**, *14*, 367-8.
(2) Farr, T. D.; Williard, J. W. *J. Chem. Eng. Data* **1971**, *16*, 67-8.
(3) Williard, J. W.; Dillard, E. F. *J. Chem. Eng. Data* **1975**, *20*, 436-7.
(4) Frazier, A. W.; Dillard, E. F.; Thrasher, R. D.; Waerstad, K. R. *J. Agric. Food Chem.* **1973**, *21*, 700-4.
(5) Muromtsev, B. A.; Nazarova, L. A. *Bull. Acad. Sci. URSS., Cl. Sci. Math. Nat.* **1938**, 177-84.
(6) Ebel, J. P. *Mikrochim. Acta* **1954**, 679-700.
(7) Karl-Kroupa, E. *Anal. Chem.* **1956**, *28*, 1091-7.

Received for review January 26, 1981. Accepted September 3, 1981.

Densities, Viscosities, and Conductances of Saturated Solutions in the Systems Mercuric Chloride–Hydrogen Chloride–Water, Mercuric Chloride–Potassium Chloride–Water, and Mercuric Chloride–Indium Chloride–Water at 25.0 °C

Elinor M. Kartzmark

Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

The densities, viscosities, and specific conductances of saturated solutions in the systems mercuric chloride–hydrogen chloride–water, mercuric chloride–potassium chloride–water, mercuric chloride–indium chloride–water were determined at 25.0 °C. The same properties were determined for aqueous solutions of indium trichloride in the concentration range 0.642–5.157 N and for mercuric chloride solutions from 0.001 N to saturation, both at 25.00 °C.

Introduction

In a previous paper (*1*), the phase diagram of the system: $HgCl_2$-$InCl_3$-H_2O was determined. The solubility curve of $HgCl_2$(s) indicates a large increase in solubility, from 6.7% to 33%, by the addition of a relatively small amount of indium chloride. This phenomenon is even more marked in the system $HgCl_2$-HCl-H_2O (*2*), where addition of ~8% HCl produces a tenfold increase in solubility. In both systems, no compound separates in the solid state, the solid phase being $HgCl_2$ anhydrous. This is in contrast to the system $HgCl_2$-KCl-H_2O where three double salts have been reported by Linke and Seidell (*3*). Here the solubility increases to 25% with the addition of 5% KCl. It may be expected that this increase in solubility of mercuric chloride would be the result of a change of the molecular species present in solution, in which case measurements of conductance and viscosity of solutions saturated with mercuric chloride (or double salt) would be of value.

Table I. Specific Conductances (κ), Densities, and Viscosities (η) of Solutions of Hydrogen Chloride Saturated with $HgCl_2$(s) at 25.0 °C

$[HgCl_2]$, wt %	[HCl] wt %	[HCl] M	density, g mL^{-1}	η^a	κ, Ω^{-1} cm^{-1}
16.4	1.53	0.487	1.160	1.121	0.1370
27.3	2.90	0.1036	1.303	1.229	0.2951
34.0	3.74	1.449	1.413	1.355	0.3817
41.0	4.56	1.926	1.540	1.541	0.4543
57.7	6.55	3.464	1.929	2.530	0.5102
65.4	8.05	5.145	2.331	5.059	0.4100
69.3	9.64	6.499	2.459	6.728	0.3620
69.2	11.0	8.373	2.776	9.441	0.3170

[a] $\eta_{H_2O} = 1.000$.

Table II. Specific Conductances (κ), Densities, and Viscosities (η) of Solutions of Indium Trichloride Saturated with $HgCl_2$(s) at 25.0 °C

$[InCl_3]$ wt %	$[InCl_3]$ M	$[HgCl_2]$, wt %	density, g mL^{-1}	η^a	κ, Ω^{-1} cm^{-1}
2.81	0.148	15.9	1.166	1.213	0.019 95
8.91	0.518	20.3	1.284	1.458	0.034 47
9.25	0.584	25.0	1.397	1.796	0.043 0
13.5	0.903	27.1	1.479	2.108	0.045 3
16.8	1.191	28.8	1.568	2.568	0.044 71
20.6	1.553	29.7	1.667	3.347	0.039 94

[a] $\eta_{H_2O} = 1.000$.

Experimental Section

In each of the three systems, several saturated solutions were prepared at 25.0 °C. The phases were separated by centrifuge at room temperature because of the high viscosity of the solutions. This introduces a small uncertainty in the temperature and therefore in the composition of the saturated solutions but would not change the nature of the solid phase(s). The liquid phases were analyzed for Hg^{2+} as HgS and then for Cl^- as AgCl. Solutions containing indium were made strongly acidic with sulfuric acid, so that indium sulfide would not separate out on addition of hydrogen sulfide. The second cation in each system was obtained by difference. The densities, viscosities, and specific conductances of the saturated solutions were measured at 25.0 °C. These data are given in Tables I-III, where the weight percentages of hydrogen chloride, potassium chloride, and indium chloride are also expressed as molarities in order to compare the properties of the saturated solutions with those of aqueous solutions of hydrogen chloride, potassium chloride, and indium chloride of the same molarities. These latter values were taken from the literature in the case of hydrogen chloride (*5*) and of potassium chloride (*6*), while

0021-9568/82/1727-0038$01.25/0 © 1982 American Chemical Society

Table III. Specific Conductances (κ), Densities, and Viscosities (η) of Saturated Liquid Phases in the System $HgCl_2$-KCl-H_2O at 25.0 °C

[$HgCl_2$]		[KCl]		density,			
wt %	M	wt %	M	g mL^{-1}	η^a	κ, Ω^{-1} cm^{-1}	nature of solid phase
9.43	0.38	0.676	0.099	1.086	1.063	0.009827	$HgCl_2$(s)
18.4	0.81	3.04	0.49	1.200	1.114	0.04168	$HgCl_2$(s)
24.9	1.19	4.77	0.83	1.294	1.150	0.06300	$HgCl_2$(s)
18.6	0.85	8.16	1.36	1.245	1.061	0.1228	$HgCl_2\cdot KCl\cdot H_2O$
20.6	0.99	11.90	2.08	1.304	1.076	0.1896	$HgCl_2\cdot KCl\cdot H_2O$
24.1	1.25	16.7	3.14	1.404	1.149	0.2576	$HgCl_2\cdot KCl\cdot H_2O$
27.4	1.50	19.9	3.98	1.490	1.252	0.3032	$HgCl_2\cdot KCl\cdot H_2O$
3.68	0.16	26.2	4.28	1.217	1.101	0.3856	KCl
9.65	0.46	26.1	4.52	1.290	1.149	0.3845	KCl
15.5	0.78	25.8	4.75	1.371	1.207	0.3826	KCl
14.8	0.74	25.4	4.64	1.363	1.205	0.3851	KCl + $HgCl_2\cdot 2KCl\cdot H_2O$
21.4	1.12	22.7	4.33	1.426	1.213	0.3389	$HgCl_2\cdot 2KCl\cdot H_2O$
19.2	0.99	23.2	4.34	1.396	1.213	0.3500	$HgCl_2\cdot 2KCl\cdot H_2O$

[a] η_{H_2O} = 1.000.

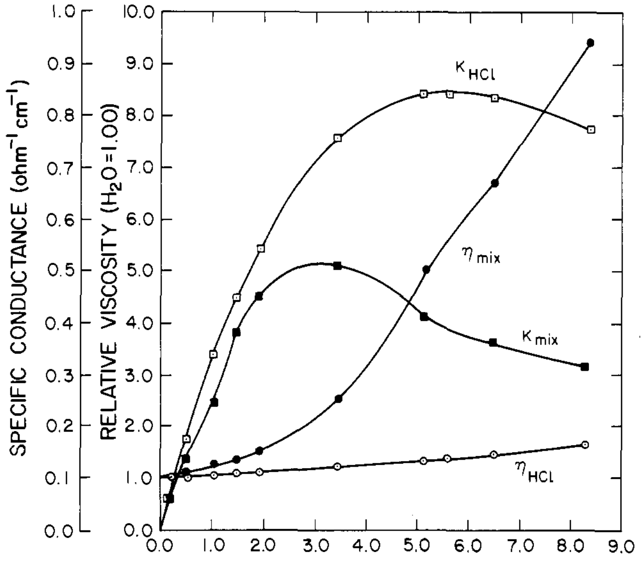

Figure 1. Viscosities and specific conductance in the system $HgCl_2$-HCl-H_2O.

the data for indium chloride and for mercuric chloride solutions were determined in this study.

The conductances of pure mercuric chloride solutions were measured at 25.00 °C in the following manner. A saturated solution of mercuric chloride (Fisher reagent grade) in conductance water (κ = 1.0 × 10^{-6}) was prepared at 25.00 °C and analyzed (6.75 ± 0.01 wt %). This stock solution was used to prepare solutions of mercuric chloride by weight dilution. Densities were determined by pyknometer at 25.00 °C. Conductances were measured in a cell, calibrated with reagent-grade potassium chloride (cell constant = 0.5436 cm^{-1}), using a Beckmann conductance bridge. The measurements were repeated by using a second stock solution (6.78 ± 0.01 wt %). The conductances, densities, and viscosities of indium chloride solutions were also determined at 25.00 °C. These data are given in Tables IV and V.

Table IV. Specific Conductances (κ), Equivalent Conductances (Λ), Densities, and Viscosities (η) of Solutions of Indium Trichloride at 25.00 °C

[$InCl_3$]		density,		κ, Ω^{-1}	Λ,
wt %	N	g mL^{-1}	η^a	cm^{-1}	Ω^{-1} cm^2 equiv^{-1}
4.58	0.642	1.0346	1.114	0.018 20	28.3
9.76	1.428	1.0776	1.247	0.028 57	20.0
13.87	2.103	1.1185	1.373	0.032 93	15.7
19.39	3.096	1.1767	1.607	0.035 53	11.5
24.54	4.107	1.2336	1.866	0.034 69	8.45
29.33	5.157	1.2967	2.254	0.031 48	6.104

[a] η_{H_2O} = 1.000.

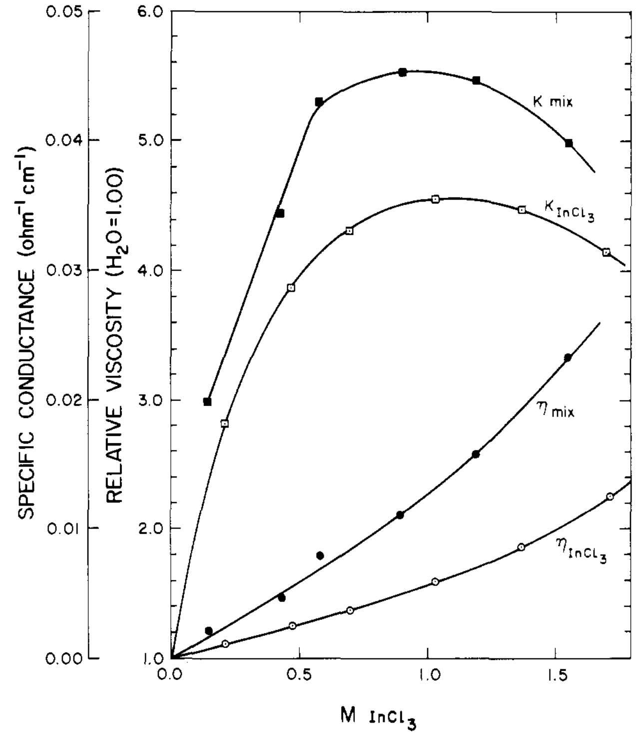

Figure 2. Viscosities and specific conductances in the system $HgCl_2$-$InCl_3$-H_2O.

Discussion

The specific-conductance values of the mercuric chloride solutions, classify the solute as a weak electrolyte, as is well-known. This indicates that the bulk of the solute is present as uncharged species in equilibrium with ions such as Hg^{2+}, $HgCl^+$, $HgCl_4^{2-}$, Cl^-, etc. When the solutions are mixed with other chlorides, the equilibrium must shift toward unconducting species so that any contribution of mercuric chloride to the specific conductances of the mixed solutions is negligible except that addition of mercuric chloride produces in every case an increase in the viscosity of the solutions and thus has an influence on their conductance. Addition of mercuric chloride to a solution of, e.g., hydrogen chloride of known molarity changes the volume of the solution and therefore changes the molarity of the hydrogen chloride in it. To compare the properties with and without mercuric chloride, I calculated the molarity of hy-

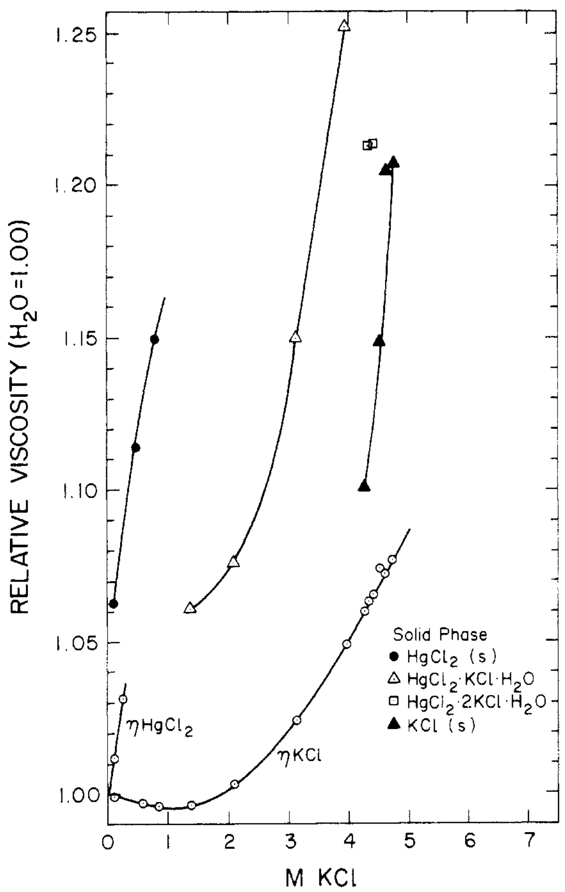

Figure 3. Viscosities in the system $HgCl_2$–KCl–H_2O.

Table V. Specific Conductances (κ), Equivalent Conductances (Λ), and Densities of Mercuric Chloride Solutions at 25.00 °C

$[HgCl_2]$ wt %	$[HgCl_2]$ N	density, g mL^{-1}	$10^3\kappa$, Ω^{-1} cm^{-1}	Λ, Ω^{-1} cm^2 $equiv^{-1}$
6.75	0.524	1.0551	0.2035	0.388
3.87	0.278	1.0278	0.1410	0.508
2.26	0.169	1.0158	0.1105	0.655
1.29	0.0955	1.0078	0.0856	0.897
1.11	0.0821	1.0066	0.0803	0.978
0.418	0.0310	1.0051	0.0548	1.770
0.213	0.0157	1.0008	0.0427	2.725
6.78	0.527	1.0559	0.2051	0.389
4.96	0.379	1.0375	0.1688	0.445
1.80	0.171	1.0165	0.1111	0.648
1.76	0.132	1.0140	0.0979	0.744
0.743	0.0547	1.0040	0.0678	1.240
0.135	0.00994	0.9981	0.0363	3.652
0.0411	0.00302	0.9980	0.0241	7.975
0.0197	0.00145	0.9980	0.0185	12.80

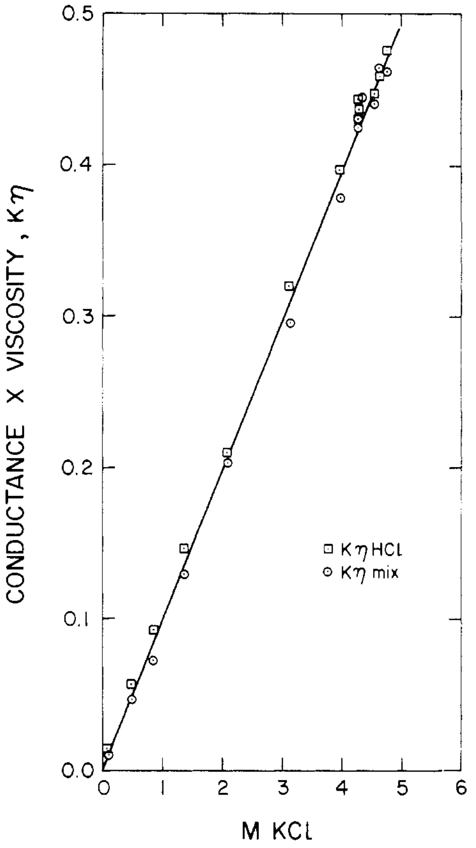

Figure 4. Conductance-viscosity product in the system $HgCl_2$–KCl–H_2O.

drogen chloride in the mixed solution. Figure 1 gives plots of viscosity and specific conductance of solutions containing mercuric chloride (η_{mix} and κ_{mix}) and those of pure HCl (η and κ). The same treatment is given the system $HgCl_2$–$InCl_3$–H_2O in Figure 2.

In Figure 1, it is seen that addition of mercuric chloride produces a large increase in viscosity of the HCl solutions, by a factor of 6 in the extreme, while for the same solution the specific conductance decreases by a factor of 2.5. The decrease in specific conductance is therefore very much less than that required by the increase in viscosity. This may be explained in terms of the Grotthus mechanism of hydrogen-ion conductance which is largely independent of the viscosity because it involves hydrogen transfer from the water rather than migration of ions through the solution.

The behavior of the system $HgCl_2$–$InCl_3$–H_2O is in sharp contrast to that of the hydrogen chloride system. Here, addition of mercuric chloride to indium chloride solution produces an increase in viscosity and at the same time an increase in the

Table VI. Ratio of Conductance-Viscosity Products

$HgCl_2$–HCl–H_2O		$HgCl_2$–$InCl_3$–H_2O		$HgCl_2$–KCl–H_2O		
[HCl], M	$\kappa\eta_{mix}/\kappa\eta_{HCl}$	$[InCl_3]$, M	$\kappa\eta_{mix}/\kappa\eta_{InCl_3}$	[KCl], M	$\kappa\eta_{mix}/\kappa\eta_{KCl}$	solid phase
0.487	0.88	0.148	1.50	0.099	0.81	$HgCl_2$
1.036	1.00	0.518	1.40	0.49	0.80	$HgCl_2$
1.449	1.07	0.584	1.88	0.83	0.78	$HgCl_2$
1.926	1.15	0.903	1.79	1.36	0.88	1:1:1
3.464	1.39	1.191	2.40	2.08	0.96	1:1:1
5.145	1.85	1.553	1.96	3.14	0.93	1:1:1
6.499	2.01			3.98	0.96	1:1:1
8.373	2.36			4.28	1.00	KCl
				4.52	0.99	KCl
				4.75	0.97	KCl
				4.64	1.01	KCl + 1:2:1
				4.33	0.96	1:2:1
				4.34	0.97	1:2:1

specific conductance, (Figure 2). These observations have been repeatedly confirmed.

Finally, the system $HgCl_2$–KCl–H_2O presents very different results from the other two. In the first place, the phase diagram is different, there being three double salts and hence five solubility curves. The equilibrium diagrams at 25 and 34 °C are reported in ref 3, but the reference for 25 °C is incorrect and therefore the author has not been able to consult the original. However, the work described for 34 °C (*7*) was done with meticulous care, leaving no doubt as to the existence of the double salts. The solubilities of this paper cooroborate those given for 25 °C and hence the formulas of the double salts were assumed to be those published.

The viscosities of the saturated solutions are plotted in Figure 3, together with those of mercuric chloride and of potassium chloride alone. In this system, where the solid phase changes, the viscosities plotted vs. molarity of potassium chloride yield a saw-toothed curve which shows some correlation with the nature of the solid phase. This suggests that the nature of the species in solution changes as the solid phase changes. When plotted vs. molarity of mercuric chloride or vs. total molarity, the same discontinuities in viscosity occur with change in solid phase. The viscosities are always greater in the saturated solution than in potassium chloride solutions of the same molarity. The specific conductances are always somewhat lower than the corresponding potassium chloride values.

When the products of specific conductance and viscosity of the saturated solutions are plotted against molarity of KCl, there is an approximately linear increase: the discontinuity accompanying change of solid phase has disappeared (Figure 4). The same behavior is observed for potassium chloride solutions of the same molarity. If the ratio of these products, viz., $\kappa\eta_{mix}/\kappa\eta_{KCl}$, is calculated, it is found to be close to unity regardless of the nature of the solid phase. This means that while the product alters with concentration, in the saturated solutions and in the potassium chloride solutions, it does so to the same extent and is independent of the nature of the solid phases. This behavior is not observed with the other two systems. See Table VI, where the ratios are given for all three systems.

Literature Cited

(1) Kartzmark, E. M. *Can. J. Chem.* **1980**, *58*, 539.
(2) Thomas, H. C. *J. Am. Chem. Soc.* **1939**, *61*, 921.
(3) Linke, W. F.; Seidell, A. "Solubility of Inorganic and Metal Organic Compounds", 4th ed.; American Chemical Society: Washington, DC, 1958; Vol. 1, p 1208.
(4) Trotman-Dickenson, A. F., Ed. Pergamon Press: Oxford, 1975; Vol. 3, p 300.
(5) Owen, B. B.; Sweaton, F. H. *J. Am. Chem. Soc.* **1941**, *63*, 2811.
(6) Chambers, J. F.; Robinson, J. M.; Stokes, R. H. *J. Phys. Chem.* **1956**, *60*, 985.
(7) Tourneux, C. *Ann. Chim.* **1919**, *11*, 225–61.

Received for review February 2, 1981. Accepted September 1, 1981.

Isobaric Vapor–Liquid Equilibria of the *p*-Xylene–1,2-Dichloroethane System

M. Venkateshwara Rao

Osmania University, Hyderabad, India

Dabir S. Viswanath*

Department of Chemical Engineering, University of Missouri-Columbia, Columbia, Missouri 65211

The vapor–liquid equilibria of the *p*-xylene–1,2-dichloroethane system were measured at 685 mmHg pressure. Vapor-pressure data in the range of 500–2700 mmHg are also reported. The results on enthalpy of mixing and vapor–liquid equilibria show that system behaves like an ideal system.

This first paper in a series on the vapor–liquid equilibrium data of *p*-xylene–chloroethane systems presents data for the *p*-xylene–1,2-dichloroethane system. Vapor–liquid equilibrium data, apart from their utility in distillation, are required to fill gaps in such important prediction methods as the UNIFAC method.

Experimental Section

Apparatus. A modified Brown still was used to collect the data. The apparatus consisted of a boiler tapered gradually to a Cottrell pump as shown in Figure 1. The boiler was heated with a nichrome wire of 60-Ω resistance. A similar heating wire was wound over the entire length of the Cottrell pump and the separating chamber. The internal heater was made of fine nichrome wire of 1.3-Ω resistance fused to tungsten leads. Figures 2 and 3 show the details of the sample trap and the monostat manometer arrangement. A cathetometer used to read the manometer allowed pressures to be read to ±0.1 mm Hg.

Purity of Materials. *p*-Xylene supplied by M/S E. Merck, Darmstadt, West Germany, was tested for thiophene, dried with phosphorus pentoxide, and then distilled twice in a 150-cm packed column. The middle fraction of the second distillation boiling at a constant temperature of 407.45 K (at 685 mmHg pressure) was collected and stored in clean, dry, amber-colored bottles.

Laboratory-grade 1,2-dichloroethane supplied by M/S BDH, Bombary, India, was washed with a dilute solution of potassium hydroxide and then with distilled water. It was then dried over phosphorus pentoxide and distilled twice. The middle fraction of the second distillation boiling at 353.15 K (at 685 mmHg) was collected and stored in amber-colored bottles. The purified substances were checked for purity by refractive index, density, boiling point at 760 mmHg, chromatograms (obtained by using an AIMIL-NCI dual-column gas chromatograph with a flame ionization detector), and NMR (obtained by using a Varian TC 60 NMR spectrometer). The purity of *p*-xylene was also checked by taking its IR spectra with a Carl Zeiss URIO spectrometer. The physical properties are tabulated in Table

0021-9568/82/1727-0041$01.25/0 © 1982 American Chemical Society