In the hexane-hexadecane-naphthalene system, there is evidence of some systematic trend in the variation of W_{123}, and this is yet more pronounced in the behavior of W'_{123}.

SUMMARY OF RESULTS IN THE TWENTY-ONE MIXED SOLVENT SYSTEMS

There are three major aspects to this series of studies:

Use of Equations 12 or 13 in Predicting Interaction. In the 10 systems for which literature values of solvent-solvent interaction are available, the average error in the prediction of solubility by either equation is 0.002 mole fraction naphthalene. In a given system, component dissimilarity is reflected in the size of the error.

Use of Equations 15 or 16 in Approximating Interaction. Treatment of a ternary system as a pseudo-binary with Equation 16 is often a useful approach. The approximation that 1–3 component interaction may be related to that of 1–2 and 2–3 by Equation 15 is similarly available. The use of these equations appears to be most valid for the aromatic pairs. Fair agreement is found for the nonaromatic pairs, while for aromatic-nonaromatic pairs, there is frequently considerable error. The assumption is generally poorest for systems involving hexadecane.

Determination of Binary Interchange Energy by Measurements in a Ternary System. In some of the systems, agreement between experimental and literature values of solvent-solvent interchange energy is quite good. Thus, the determination of that quantity by solubility measurements in solvent-solvent mixtures is a suitable method in systems behaving regularly and with pairwise interaction.

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NOMENCLATURE

ΔG^E = molar excess Gibbs free energy of mixing
$\overline{\Delta G}{}_2^E$ = solute partial molar excess Gibbs free energy of mixing
$\overline{\Delta G}{}^E_{2\text{binary}, x}$ = $\Delta\overline{G}{}_2^E$ calculated with Equation 12
$\overline{\Delta G}{}^E_{2\text{binary}, \phi}$ = $\Delta\overline{G}{}_2^E$ calculated with Equation 13
V° = molar volume
W = interchange energy, cal. mole^{-1}
W' = interchange energy, cal. ml.$^{-1}$
x = mole fraction
x° = mole fraction, solute-free basis
δ = solubility parameter
γ = activity coefficient
ϕ = volume fraction
ϕ° = volume fraction, solute-free basis

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Conductivity of Silver Nitrate in Nonaqueous and Mixed Solvents

R. E. BUSBY
Brunel College, Woodlands Avenue, Acton, London, W. 3

V. S. GRIFFITHS
Battersea College of Technology, Battersea, London, S.W. 11.

Measurements of the conductivity of silver nitrate in methanol and binary mixtures of methanol containing 0.1 mole % of nitromethane, pyridine, and benzene at 30° C. are reported and discussed.

SOLVENT-ION EFFECTS have been observed in previous conductivity work (*1*) at 25° C. with silver nitrate in methanol containing an electron-donating additive, present in an amount (0.1 mole %) sufficient to interact appreciably with the cation but not to alter the viscosity and dielectric constant of the main solvent effectively. The conductivity of silver nitrate in methanol and binary solvent mixtures was measured at 30° C. Each mixture contained 99.9 mole % methanol and 0.1 mole % of one of the additives used previously (*1*), namely, pyridine, nitromethane, and benzene. This provided thermodynamic data to extend knowledge on solvent-ion interaction.

EXPERIMENTAL

Procedure. A Hartley-Barrett-type cell (*10*), made of borosilicate glass and fitted with greyed-platinum electrodes, was used for these investigations. Conductivities were measured at 30 ± 0.005° C. with a bridge arrangement similar to that described by Davies (*3*), except that the oscillator and detector were contained in one instrument supplied by Airmec Laboratores Ltd., England. A frequency of 1 kc. per second was used for most measurements, but occasionally this was varied to ensure that polarization effects were absent.

All solutions were made up by weight. The solid was weighed in an atmosphere of pure, dry nitrogen, and the tube and contents were introduced into a 1.5-liter flask. The requisite quantity of solvent was "blown over" into the flask with pure, dry nitrogen. Normally, solutions were stored for a few days only. Weighed quantities of electrolyte solution were added from a weight pipet to a known weight of the solvent in the cell. The addition was repeated four or five times for each "run." All-glass borosilicate apparatus was used. All these operations and the conductivity measurements themselves were carried out in subdued light, when silver nitrate was the electrolyte used.

Materials. The determination of the cell constant was carried out using potassium chloride solutions in water, the specific conductivity of which was less than 0.2×10^{-6} ohm^{-1} cm.$^{-1}$. Potassium chloride and silver nitrate were each recrystallized four or five times from such conductivity water.

Table I. Conductivities of Silver Nitrate at 30° C.

10^4C	Λ	10^4C	Λ
Pure methanol		99.9 mole % methanol–0.1 mole % nitromethane	
1.5222	113.91	1.0105	114.61
1.7019	113.79	1.2441	114.48
2.5285	112.44	2.0603	112.91
3.4897	111.01	2.2300	112.69
4.0655	110.37	3.0497	111.66
4.2932	110.02	3.4923	111.04
5.1185	109.09	4.1846	110.24
5.5198	108.70	4.2645	110.08
6.6101	107.55	5.3710	108.87
6.7757	107.38	5.3795	108.90
8.0142	106.17	6.2526	108.01
8.2547	106.08	6.5499	107.68
99.9 mole % methanol–0.1 mole % pyridine		99.9 mole % methanol–0.1 mole % benzene	
4.1218	109.19	1.0735	113.86
4.5203	108.65	1.6372	113.45
4.8034	108.34	1.8572	112.65
5.1443	108.00	2.3202	112.20
6.0186	107.06	2.7600	111.52
6.9143	106.30	3.6186	110.48
7.0172	106.15	3.7956	110.36
8.5092	105.05	4.4296	109.55
...	...	5.0487	108.86
...	...	5.8837	107.95

Gillo's method (*7*) was used for the purification of methanol, and in the final stages of purification, the methanol was distilled at least twice from sodium. The specific conductivity was lower than 0.02×10^{-6} ohm^{-1} cm.$^{-1}$.

Pyridine was purified by the method of Griffiths (*9*), and benzene by the method of Rybicka and Wynne-Jones (*11*). Nitromethane was treated with calcium chloride and distilled once only. Samples of each of these were stored under nitrogen in sealed ampoules until used.

RESULTS

Accuracy. A small correction was made for the dielectric constant in the case of solvent mixtures, assuming a linear relationship to hold between the composition of the appropriate mixture and dielectric constant. The same value of the viscosity coefficient (0.0054523 poise) for methanol was used in every case, the maximum probable error in the final Shedlovsky Λ_0 value being less than 0.01%.

Values of Λ were reproducible to within 0.04%. This is barely within the limits of error necessary to give much meaning to Λ_0 and K_A values calculated by the method of Fuoss (*6*). Therefore, Fuoss Λ_0 and K_A values are not included.

Tables and Diagrams. Table I shows the equivalent conductivities at the respective concentrations of silver nitrate at 30° C. Values of Λ_0 and K_A at 30° C., calculated by the method of Shedlovsky (*12*), are given in Table II.

Values of ΔH, ΔF^0, and ΔS^0 at 25° C. for the ionic equilibria of silver nitrate were calculated from the expressions (*8*):

$$\log \frac{K_{A^1}}{K_{A^2}} = -\frac{\Delta H}{4.576}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where K_{A^1} and K_{A^2} represent the association constants at temperatures T_1(298°) and T_2(303°), respectively (*2*):

$$\Delta S^0 = \frac{(\Delta H - \Delta F^0)}{T_1}$$

where $\Delta F^0 = RT_1 \ln K_{A^1}$.

Shedlovsky Λ_0 and K_A values, obtained at 30° C. as described above and in a similar manner at 25° C. (*1*), were used to calculate ΔH, ΔF^0, and ΔS^0.

DISCUSSION

The Λ_0 and K_A values show that—as at 25° C. (*1*)—addition of a small amount of pyridine to methanol decreases the mobility of the silver ion and the extent of association of silver and nitrate ions. This variation is less pronounced than at 25° C. (*1*). Assuming Λ_0 to be a function of the effective size of the conducting species, a decrease in association should, as observed here, accompany an increase in ion size. If the theory of water-ion interaction outlined by Frank, Evans, and Wen-Yang Wen (*4, 5*) holds for

Table II. Equivalent Conductivities at Infinite Dilution of Silver Nitrate at 30° C. and Constants for Silver Nitrate Equilibria at 30° C.

Solvent	Λ_0 (*12*)	K_A (*12*)	ΔH(Cal.)	ΔF^0(Cal.)	ΔS^0 (Cal./Deg.)
Pure methanol	118.55	83	−4,210	+2,550	−23
99.9 Mole % methanol–0.1 mole % pyridine	116.75	68	−4,410	+2,530	−23
99.9 Mole % methanol–0.1 mole % nitromethane	118.43	79	+200,000 approx.	+6,000 approx.	+700 approx.
99.9 Mole % methanol–0.1 mole % benzene	118.13	81	−2,180	+2,140	−80

methanol, the extent of (*a*) solvent molecule immobilzation in the immediate vicinity of an ion, and (*b*) solvent structure disruption beyond the periphery of the ionic species, will determine the extent of any net structure-making or -breaking effect. In the presence of pyridine, (*a*) appears to offset (*b*) more than when nitromethane or benzene are present, or when no additive is present. The small reduction in mobility observed here in the presence of benzene is about the same as that observed at 25° C. (*1*).

The values of ΔH, ΔS^0, and ΔF^0 for the equilibrium of silver nitrate in methanol, and in the presence of the additives pyridine and benzene, are consistent with the exothermic nature of the solvation process. However, solvation in the presence of nitromethane appears to be an endothermic process. This is brought about by silver nitrate behaving as a much weaker electrolyte at 25° than at 30° C. At 25° C., there is much greater ionic mobility at infinite dilution in the presence of nitromethane than when either pyridine or benzene is present or in the absence of an additive (*1*); whereas at 30° C., only a small diminution in Λ_0 is observed. Thus the extent—and perhaps nature—of solvation has, in the course of a 5° rise in temperature, undergone a profound change. A number of explanations could be advanced for this, but only two will be mentioned here. The silver ion may, more or less, be permanently solvated mainly by nitromethane at 25° C., whereas at 30° C. methanol largely replaces nitromethane in this role. Also, the silver ion at 25° C. may not be permanently solvated by either nitromethane or methanol, whereas at 30° C. permanent solvation, mainly owing to silver ion-methanol interaction occurs. Both these suggestions imply that, in the presence of nitromethane, the effective bonding between solvent molecules, within the solvate sheath and those in the bulk of the solvent, is more important at 30° than at 25° C.—i.e., any dragging effect involving long range forces should be more pronounced at the higher temperature. However, more data are needed at other temperatures to make any explanation more conclusive.

NOMENCLATURE

Λ_0 = limiting equivalent conductivity of electrolyte, silver nitrate, at infinite dilution
Λ = equivalent conductivity of electrolyte, silver nitrate
K_A = association constant
ΔH = heat of dissociation in calories
ΔS^0 = entropy of dissociation, in calories, at unit activity
ΔF^0 = free energy of dissociation, in calories, at unit activity
c = concentration of electrolyte, silver nitrate, in moles per liter of solution

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Phase Transition on Submicron Particles of ZrO_2

F. W. VAHLDIEK
Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio

Spherical submicron particles of ZrO_2 were a mixture of 50% monoclinic and 50% tetragonal ZrO_2. The metastable tetragonal phase transformed to the monoclinic phase when samples were heated to 820° C. for 2 hours. The transitions of the as-received ZrO_2 samples determined by high temperature x-ray diffraction and differential thermal analysis methods were from 1000° to 1190° C. (increasing temperature, endothermic) and 1040° to 300° C. (decreasing temperature, exothermic). The transformations for specimens preheated to 1450° C. were from 1110° to 1205° C. (increasing temperature) and from 980° to 895° C. (decreasing temperature)

POLYMORPHIC TRANSITION encountered in ZrO_2 has been studied by many investigators (*2, 5, 6, 7, 9*). Recently, the high temperature tetragonal phase was stabilized to room temperature by pressures of 15 to 20 kbars at temperatures of 1200° to 1700° C. (*8*). The reversible monoclinic-tetragonal transition of ZrO_2, which is associated with a destructive volume change makes its higher temperature applications very difficult. This transition occurs rapidly with increasing temperature at 1193° to 1205° C. and with decreasing temperature at 1050° to 1000° C. (*3, 4*). Baun (*1*) found by high temperature x-ray diffraction on spectrographic grade ZrO_2 (99.95% pure), a transition temperature range from 1000° to 1200° C. with increasing temperature, and from 980° to 750° C. with decreasing temperature.

EXPERIMENTAL

Spherical submicron particles of ZrO_2 (99.7% pure with 0.1% carbon as the major impurity), as-received from Vitro Laboratories with an average particle size distribution of 0.04 micron, were used in studying this transformation. These particles were prepared by a carbon arc vaporization - sublimation process using monoclinic ZrO_2 powders (325 mesh) as starting materials. Table I shows the principal impurities of a typical sample and the impurity distribution of a sample heated to 820° C. in air for 2 hours using a platinum boat.

Subsequent x-ray diffraction analysis using Co Kα radiation indicated the particles to be a mixture of 50% monoclinic–50% tetragonal ZrO_2. The percentage of monoclinic