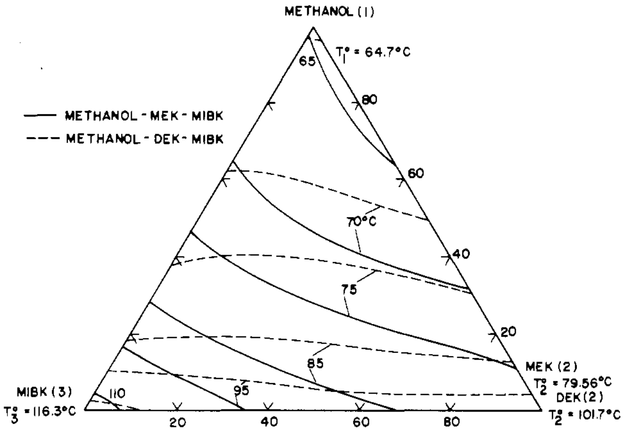

Figure 1. Isotherms for methanol–MEK–MIBK and methanol–DEK–MIBK at 760 mmHg.

quired in direct correlation and 18 parameters are required when all binary parameters are taken into account. Alternatively, with 12 parameters (for methanol–DEK–MIBK) the mean deviation for direct correlation is 0.52%, whereas with 15 parameters the mean deviation is 0.68% taking into account the binary information.

Isotherms (Figure 1) were calculated on the basis of eq 18, and the parameters reported in Table VI. The shape of the curves indicates that that system does not exhibit azeotropic behavior.

Acknowledgment

Yehudit Reizner helped in the experimental work.

Glossary

A_{ij}, B_{ij}, etc.	multicomponent adjustable parameters in Redlich–Kister or Wilson expansions
A_i, B_i, C_i	parameters in Antoine's equation; eq 13
a_{ir}, a_{jr}	adjustable parameters in eq 7
C_1	ternary constant
c'	total number of parameters per binary system
c	total number of parameters which correspond to the mixture of the highest order (ternary) system
$\bar{D}$	mean overall deviation from observed values; eq 10
DEK	diethyl ketone
M	intensive property; $M = T$ or Y
MEK	methyl ethyl ketone
MIBK	methyl isobutyl ketone
m	total number of data points which correspond to the system of the highest order
N	number of components in a mixture
P	total pressure
P_i^0	vapor pressure of pure component i
V_i^l	liquid molar volume of component i
T	absolute temperature
T_i^0	boiling temperature of pure component i
t	temperature in °C
X_i, Y_i	mole fraction of component i in the liquid and vapor phases
Y	local deviation from observed values; $Y = (Y_{obsd} - Y_{calcd})/Y_{obsd}$
α_{ij}	separator factor; eq 6
γ_i	activity coefficient of component i
σ^2	error variance; eq 9
ΔX, ΔP, Δt	errors in measurements of concentration, pressure, and temperature

Subscripts and Superscripts

calcd	calculated
obsd	observed
l	liquid phase
i	component i
max	maximum
min	minimum

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Transference Numbers for KCl in Ethanol–Water Mixtures at 25 °C

Miguel A. Esteso* and Domingo M. Grandoso

Departamento de Química Física, Universidad de La Laguna, Tenerife, Canary Islands, Spain

Cation and anion transference numbers for KCl at different ionic concentrations in 5, 10, 20, and 30 wt % ethanol–water mixtures at 25 °C are determined by the direct moving boundary method. Limiting cation transference numbers, T_+^0, are obtained by using the various Fuoss–Onsager and Pitts' equations and verify the earlier data of Fratiello and Kay. The variation of these T_+^0 values with the ethanol content in the mixture was analyzed as a function of a selective solvation effect on both K^+ and Cl^- ions in these media.

Introduction

In a previous paper by this laboratory (*1*) cation and anion transference numbers for KCl in 10 wt % ethanol–water mixture were obtained to establish which of the two sets of existing data (*2*, *3*) was correct. Because the biggest differences between them are from the 15 wt % ethanol–water mixture, we realized the necessity of obtaining some other points which would help us in this purpose.

Experimental Section

The quality of the chemicals and solvents used, their purifi-

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Table I. Summary of Transference Numbers Observed and Corrected for KCl in Ethanol-Water Mixtures at 25 °C

wt % EtOH	C, equiv dm^{-3}	i, mA	T_+	T_-	$10^4\Delta T_{\mathrm{vol}}$	$10^4\Delta T_{\mathrm{sol}}$	$(T_+)_{\mathrm{cor}}$	$(T_-)_{\mathrm{cor}}$	$(T_+)_{\mathrm{c}} + (T_-)_{\mathrm{c}}$
5	0.020 01	0.71–0.76	0.4957_9		–1.5	2.1	0.4961_4		1.0000_6
		0.66–0.80		0.5038_6	–1.5	2.1		0.5039_2	
	0.049 96	1.41–1.81	0.4958_4		–1.0	0.9	0.4960_3		1.0000_3
		0.81–2.00		0.5040_1	–1.0	0.9		0.5040_0	
	0.100 03	2.27–2.52	0.4969_3		0.5	0.5	0.4969_3		1.0006_0
		2.25		0.5035_7	0.5	0.5		0.5036_7	
10[a]	0.020 01	0.61–0.91	0.5018_2		1.0	1.8	0.5019_0		1.0002_0
		0.71–0.95		0.4980_3	1.0	1.7		0.4983_0	
	0.049 99	0.72–1.60	0.5019_7		1.7	0.7	0.5018_7		1.0001_1
		1.10–2.01		0.4980_0	1.7	0.7		0.4982_4	
	0.099 84	1.31–2.01	0.5020_7		2.1	0.4	0.5019_0		(1.0002_0)
20	0.019 94	0.65–0.76	0.5085_1		0.1	1.8	0.5086_8		1.0003_3
		0.86–0.91		0.4914_7	0.1	1.7		0.4916_5	
	0.050 00	1.21–1.61	0.5089_1		0.3	0.7	0.5089_5		1.0004_5
		1.36–1.50		0.4914_0	0.3	0.7		0.4915_0	
	0.100 00	1.61–2.25	0.5086_0		0.5	0.4	0.5085_9		1.0002_4
		1.61–2.20		0.4915_6	0.5	0.4		0.4916_5	
30	0.050 02	1.00–1.51	0.5088_9		0.3	1.6	0.5090_2		1.0000_5
		0.96–1.10		0.4908_5	0.3	1.5		0.4910_3	
	0.075 00	1.60–1.80	0.5091_4		0.2	1.1	0.5092_3		1.0005_9
		1.54–1.65		0.4912_4	0.2	1.0		0.4913_6	
	0.099 38	1.72–1.90	0.5088_1		–1.2	0.8	0.5090_1		1.0000_9
		1.56–1.76		0.4911_2	–1.2	0.8		0.4910_8	

[a] Reference *1*.

cation, and the solution preparation technique have been described elsewhere (*1*), as well as the apparatus for the direct moving boundary technique.

Results and Discussion

The transference numbers obtained are shown in Table I. Because no influence of the current on transference numbers was observed, the $T_\pm$ values are average values. In the cation runs LiCl was used as following solution, while $KCOOCH_3$ was used in the anion runs.

The volume correction, $\Delta T_{\mathrm{vol}} = C\Delta V$, where $\Delta V = \bar{V}(\mathrm{AgCl}) - \bar{V}(\mathrm{Ag}) - T_{\mathrm{K}^+}{}^{\mathrm{KCl}}\phi_{\mathrm{KCl}}$ (in cm^3 equiv^{-1}) is negative in the cation runs and positive in the anion runs.

The solvent correction is given by

$$\Delta T_{\mathrm{sol}} = [(T_{\mathrm{obsd}})_\pm \pm C\Delta V](\kappa_{\mathrm{solv}}/\kappa_{\mathrm{solute}})$$

and was calculated from known conductance data (*4*). Both volume and solvent corrections are shown in Table I.

The sum $(T_+)_{\mathrm{cor}} + (T_-)_{\mathrm{cor}}$ is given in Table I. As can be seen, there are no important differences between these and the theoretical unity value. Dividing each cation (or anion) transference number by this sum, we determined the *best* transference numbers (Table II).

The correction for the electrophoretic effect in order to obtain the limiting transference numbers, $T_\pm{}^0$, was made by simultaneously applying the 1957 Fuoss-Onsager $(FO)_1$ equation, the 1963 $(FO)_2$ equation, and the Pitts (P) equation to these *best* values, whose mathematical expressions are respectively

$$T_\pm{}^0 = T_\pm - \frac{(T_\pm - 0.5)B_2C^{1/2}}{\Lambda^0(1 + y)} \tag{1}$$

$$T_\pm{}^0 = T_\pm - \frac{(T_\pm - 0.5)(B_2C^{1/2} - B_3)}{\Lambda^0} \tag{2}$$

$$T_\pm{}^0 = T_\pm - \frac{(T_\pm - 0.5)Y_3}{\Lambda' + Y_3} \tag{3}$$

where B_2, B_3, Λ', and Y_3 are functions of solvent parameters, of a (the distance of closest approach between cation and anion, in angstroms), and of standard amounts. The procedure of applying these equations was, in accord with Sidebottom and Spiro (*5*), the following: varying a until the $T_+{}^0$ values, calculated from the data points at the different concentrations, are equal within experimental error. These values of $T_+{}^0$ are given in Table II with an indication of the equation used.

Table II. Summary of "Best" and Limiting Cation Transference Numbers and Ionic Conductances for KCl in Ethanol-Water Mixtures at 25 °C

wt % EtOH	C, equiv dm^{-3}	T_+	$T_+{}^0$ $(FO)_1$	$T_+{}^0$ $(FO)_2$	$T_+{}^0$ (P)	Λ^0	$\lambda_+{}^0$
5	0.020 01	0.4961	0.4964	0.4961	0.4964	128.05_7	63.52_7
	0.049 96	0.4960					
	0.100 03	0.4966					
10	0.020 01	0.5018	0.5018	0.5017	0.5018	109.53_1	54.95_5
	0.049 99	0.5018					
	0.099 84	0.5018					
20	0.019 94	0.5085	0.5083	0.5083	0.5083	82.23_1	41.79_8
	0.050 00	0.5087					
	0.100 00	0.5085					
30	0.050 02	0.5090	0.5086	0.5085	0.5087	66.09_4	33.61_0
	0.075 00	0.5089					
	0.099 38	0.5090					

As can be seen (Table II), the $T_+{}^0$ values obtained by using eq 1–3 are so close that only slight differences are found between them. Nevertheless, the values of the parameter a from which these $T_+{}^0$ values are calculated have a more physical meaning in the case of $(FO)_2$ (5 Å $< a <$ 10 Å) than in the other two equations ($a >$ 10 Å). Therefore it can be accepted that eq 2 is the best to describe KCl in these ethanol-water mixtures.

The $T_+{}^0$ values obtained from eq 2 in the present work are represented in Figure 1, against wt % of ethanol, together with Fratiello and Kay values (*2*), which agree completely with our overall values for these mixtures, and Erdey-Gruz and Majthenyi values (*3*) which exhibit an analogous tendency to that of the former in the diluted part but differ appreciably from them above 15 wt % of ethanol.

The three data series are similar in the water-rich region, where the K^+ ion has an increase in its mobility larger than that of the Cl^- ion, showing a maximum value at ~25 wt %, which cannot be justified as a viscous effect or as something due to the different structure-breaking character of both K^+ and Cl^- ions only. One possible explanation of this behavior can be tried, in accord with Frank (*6*), by using the concept of selective solvation of the ions in these ethanol-water mixtures. If there

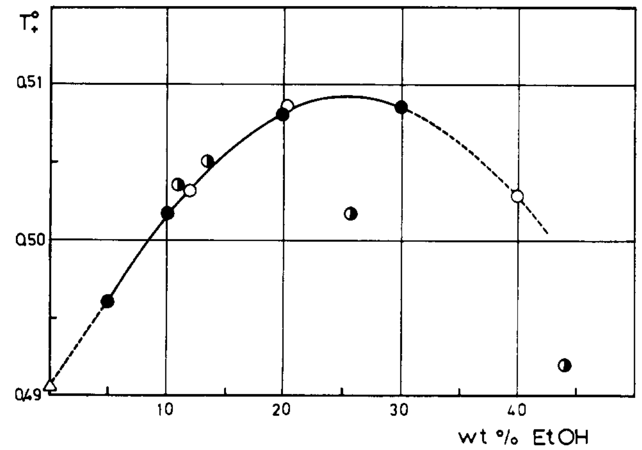

Figure 1. Variation of the limiting cation transference numbers with wt % of ethanol: (●) present work; (○) ref *2*; (◑) ref *3*; (△) ref (*7*).

is a greater amount of water in the cosphere of the ion with respect to the bulk solvent, the microscopic viscosity around the ion falls and the mobility of the ion increases (ascending line in Figure 1). On the contrary, a greater amount of ethanol in the cosphere of the ion with respect to the bulk solvent should increase the viscosity around the ion, and, therefore, its mobility should diminish (descending line in Figure 1).

From the $T_+{}^0$ values in the present work (by using eq 2) and the limiting equivalent conductances, Λ^0, known previously (*4*), limiting ionic conductances have been determined (Table II).

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NEW COMPOUNDS

3-(Arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines: Oxidative Debenzylation and Cyclization of 1-(Phenylbenzylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets

P. K. Srivastava* and S. K. Rai
Department of Chemistry, Banaras Hindu University, Varanasi—221005, India

V. K. Verma
Applied Chemistry Section, Institute of Technology, Banaras Hindu University, Varanasi—221005, India

A number of 3-(arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines have been synthesized by the oxidative debenzylation and cyclization of the corresponding 1-(phenylbenzylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets. The characterization of these compounds has been achieved by the direct oxidation of the corresponding 2,4-dithiobiurets and also by IR spectra.

Oxidation of 2,4-dithiobiurets to the related 1,2,4-dithiazolidines has been a well-known method (*1–6*) of synthesis. Recently, it has been reported that substituted 1,2,4-dithiazolidines could also be synthesized by the oxidative dealkylation of the related isodithiobiurets (*7–12*). In light of these observations, it was thought of interest to extend the oxidative debenzylation and cyclization reaction to the synthesis of certain hitherto unreported 3-(arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines.

This paper describes the synthesis of certain new 3-(arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines by the oxidative debenzylation and ring closure of the related 1-(phenylbenzylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets. The reaction can be represented as shown in Scheme I.

Experimental Section

Melting points were determined by a Kofler hot stage apparatus and are uncorrected.

Benzophenone thiosemicarbazone (I) was prepared by the known procedure (*13*) and its *S*-benzyl derivative (II) was obtained by benzylation with benzyl chloride in the presence of sodium ethoxide (*14*).

1-(Phenylbenzylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets (III). The details of a typical experiment are as follows: Benzene solution of *S*-benzylisobenzophenone thiosemicarbazone (3.43 g) was refluxed with phenyl isothiocyanate (1.35 g) for 1 h. On evaporation of the solvent, 1-(phenylbenzylideneamino)-5-phenyl-2-*S*-benzyliso-4-thiobiuret was obtained as a semisolid, which on washing with petroleum ether and on addition of a little ethanol became granular; mp 98 °C (yield 3.5 g, 75%). The results of these experiments are summarized in Table I.

3-(Arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines (V). (I) Oxidative Debenzylation of 1-(Phenylbenzylideneamino)-5-aryl-2-S-benzyliso-4-thiobiurets. The

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