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Transference Number Measurements for LiBr in Ethanol–Water Mixtures at 25 °C

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Transference numbers for both ions of LiBr in ethanol–water mixtures up to 85 wt % ethanol at 25 °C are obtained. The experimental technique used for these measurements is the direct moving boundary. These transference numbers, after the volume and the solvent corrections are applied, are optimized from the unity value of their sum at each concentration studied and the T_{best} values obtained. Afterward these optimized transference number values are also used to optimize the concentration value C_{best} for the different LiBr solutions used. The extrapolation of these T_{best} to zero concentration values to find the limiting transference number values, T°, is made by using the 1963 Fuoss and Onsager electrophoretic term. These T° values are analyzed with respect to the change of the ethanol content of the medium. Finally, ionic limiting conductance values are determined.

Introduction

The use of mixed solvents is a common practice to study the properties of electrolytes in solution. In fact, the important changes the ion–solvent interaction undergoes as a consequence of the competitive presence of two solvents in the medium leads to important structural alterations in both the solvated ions and the medium, which can be analyzed by means of the changes that occur in both the thermodynamic and the transport properties of the ions present in the solution. From among such mixed solvents, the water–organic solvents have been extensively used due to the high solubility that enables such studies to be extended to a wide concentration range for a large group of electrolytes. Nevertheless, the determination of transport parameters in these media has received no special attention from researchers, and only a small number of these transport parameters are collected in the literature.

In the present paper, transference numbers for both ions of LiBr in ethanol–water mixtures, up to 85 wt % ethanol are reported. One of the main difficulties encountered was measuring accurately the concentration of the LiBr solutions used. However, the experimental determination of such transference numbers independently for both the anion and the cation avoided this difficulty by optimizing them and afterward optimizing also the solution concentration.

Experimental Section

Chemicals and Solvents. LiBr, Merck "suprapur", was heated in vacuo at 150 °C for 72 h before use. $(C_2H_5)_4NBr$, Carlo Erba for Polarography, was used as supplied; it was dried by using a dry nitrogen stream just before being used. $KOOCCH_3$, Merck analytical reagent grade, was recrystallized twice from a saturated solution with ethanol, dried in an oven at 110 °C for 24 h, and then stored in a desiccator.

As solvent, both conductivity-grade water ($\kappa_0 = 5 \times 10^{-7}$ ohm^{-1} cm^{-1} at 25 °C) and Merck analytical-reagent-grade ethanol distilled once (*1*) ($\kappa_0 = 8 \times 10^{-9}$ ohm^{-1} cm^{-1} at 25 °C) were used.

Solutions. LiBr leading solutions were made from aqueous stock solutions. The procedure followed to prepare and determine the concentration of these stock solutions was described in a previous paper from this laboratory (*2*). On this occasion, however, two different expressions, obtained by fitting density–concentration data reported in the literature (*3*)

$$d = (0.997055 \pm 3.4 \times 10^{-5}) + (0.00726 \pm 2.6 \times 10^{-5})p \qquad (1)$$

and

$$d = (0.997071 \pm 3.0 \times 10^{-6}) + (0.00717 \pm 3 \times 10^{-6})p + (0.0000425 \pm 4 \times 10^{-7})p^2 \qquad (2)$$

(p being wt % anhydrous LiBr corrected to in vacuo), were used to replace the experimental measured density of each solution. These expressions depended on whether the solution was diluted (up to 2 wt % LiBr) or concentrated.

By taking a very accurately weighed portion of a determinated aqueous stock solution and adding to it the adequate amounts, corrected to in vacuo, of both water and ethanol, the different leading solutions of LiBr were prepared. The concentration of each leading solution was first ascertained as weight percent of its various components together with the value of its corresponding confidence intervals for a confidence of 95%. This concentration value was afterward translated to molality and finally to molarity by using the Robinson and Stokes equation (*4*):

$$\frac{C}{m} = \frac{d}{1 + 10^{-3}mM} \qquad (3)$$

where d is the experimental measured density of this solution and M the molecular mass of LiBr (86.85).

Apparatus. The apparatus and the direct moving boundary technique used were previously described (*2*).

Results

The summary of the observed and corrected transference numbers for both ions is presented in Table I. In the first column the molar concentration of each solution is presented together with its calculated confidence interval, and in the second, the electrolytic current range used is presented. At least three runs were carried out at different electrolytic currents for each solution studied; these measurements in the current intervals were reproducible with differences of less than 1 part in 1000. Therefore, the observed transference numbers presented in this table are the mean values in these intervals.

The volume correction, $\Delta T_{\mathrm{vol}} = C\Delta V_\pm$, was calculated, in all cases, from

$$\Delta V_\pm = \bar{V}(\mathrm{AgBr}) - \bar{V}(\mathrm{Ag}) - T_+(\mathrm{LiBr})\ \Phi(\mathrm{LiBr}) \qquad (4)$$

$\bar{V}$ and Φ being molar and apparent molar volumes, respectively. The values substituted in eq 4 were 29.01 and 10.27 cm^3 mol^{-1} for the molar volumes of AgBr and Ag, respectively. The apparent molar volumes were calculated by using the expression

$$\Phi = \frac{1000}{Cd_0}(d_0 - d) + \frac{M}{d_0} \qquad (5)$$

in which d_0 and d are the experimental densities of the pure

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solvent mixture and the corresponding solution at C molar concentration, respectively.

The values for these volume corrections are presented in Table I. They must be substracted from the observed transference numbers in the case of the cation runs and added to them in the case of anion runs.

The solvent correction, $\Delta T_{solv} = [(T_{obs})_\pm \mp \Delta T_{vol}](\kappa_{solv}/\kappa_{solute})$, was calculated at each C concentration by using the specific conductivity values which were derived from their equivalent conductance in the corresponding ethanol–water mixture. The expressions used for the calculation of these equivalent conductances were

$$\begin{aligned}
\Lambda &= 82.45 - 63.32C^{1/2} + 38.68C \log C \quad (10\%) \\
\Lambda &= 61.29 - 50.10C^{1/2} + 38.28C \log C \quad (20\%) \\
\Lambda &= 42.93 - 43.89C^{1/2} + 50.27C \log C \quad (40\%) \\
\Lambda &= 38.49 - 53.94C^{1/2} + 93.66C \log C \quad (60\%) \\
\Lambda &= 37.60 - 90.28C^{1/2} + 264.04C \log C \quad (85\%)
\end{aligned} \tag{6}$$

at the different ethanol–water mixtures indicated in parentheses. These expressions were obtained from published data (*5*). The values of these solvent corrections are also presented in Table I and must always be added to the observed transference numbers.

The corrected transference numbers for both the cation and the anion are summarized in Table I. Their sums at each concentration of LiBr studied in each ethanol–water mixture are shown in Table II. These sums differ from the theoretical unit value, but their discrepancies can easily be minimized by dividing each of these corrected values by the corresponding sum. Thus the *best* value for the transference number at the mentioned concentration is obtained. These *best* values are shown in Table II for the cation only.

The discrepancies found for these sums of corrected transference numbers with respect to the unit value were analyzed, as was done in aqueous solutions (*2*), to estimate the error that could have been introduced into the concentration values used in the calculation. These errors in concentration are shown in Table II together with the *best* concentration values.

The calculation of limiting transference number values when the *best* concentration of LiBr approaches zero, $T°$, was made by using the equation

$$T°_\pm = T_\pm - \frac{(T_\pm - 0.5)(B_2C^{1/2} - B_3)}{\Lambda°} \tag{7}$$

obtained from the 1963 Fuoss and Onsager electrophoretic term (*6*), for which

$$B_2C^{1/2} = e^2\chi N/3\pi\eta$$

$$B_3 = (e^4N\chi^2/12\pi\eta DkT)F(b)$$

$F(b)$ is a function of the Bjerrum parameter, $b = e^2/aDkT$, whose value is calculated for each a value (a being the closest approach cation–anion parameter); χ^{-1}, the Debye radius, and all the other symbols have their usual meaning.

The values thus obtained for $T°_+$ and a parameters are presented in Table III. The necessary values in eq 7 were taken from the literature (*5*).

Since $\lambda° = T°\Lambda°$, this equation applied to both the anion and the cation, afterward rearranged suitably, gives the expression

$$\lambda°(\mathrm{Li}^+) = \lambda°(\mathrm{Br}^-)\frac{T°(\mathrm{Li}^+)}{T°(\mathrm{Br}^-)} \tag{8}$$

which enables the equivalent conductance for the lithium ion, at the different ethanol–water mixtures used, to be calculated. For this purpose we took the values of $\lambda°(\mathrm{Br}^-)$ reported in the literature (*5*, *7*). The values of the conductances obtained are summarized in Table III.

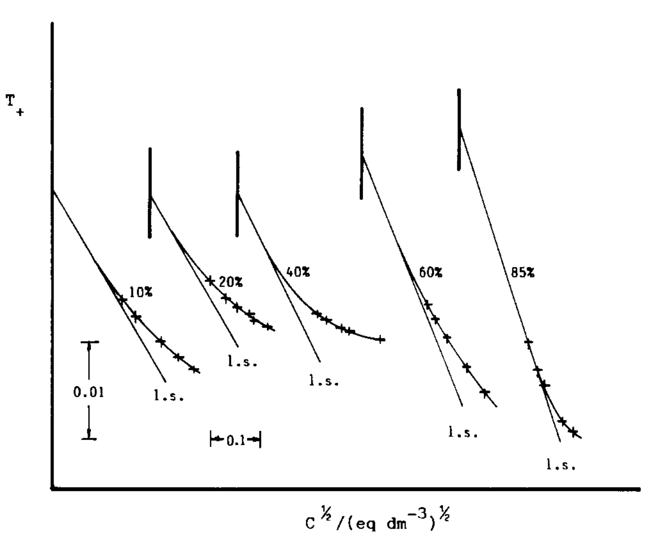

Figure 1. Concentration dependence on T_+ values in different ethanol–water mixtures studied (l.s. means limiting slope, in accordance with ref *8*).

Discussion

As can be seen in Table II, in all cases the sum of the transference numbers, after the volume and the solvent corrections, differs greatly from the unity value as it occurred in the aqueous LiBr solutions (*2*). The explanation of these wide discrepancies must be looked for in the concentration values of the LiBr solutions used. In fact, these concentration values correspond to the mean of the confidence intervals assumed (95% of confidence) for the determination of such concentrations. However, due to the hygroscopic nature of this electrolyte, we are not sure that these mean values are coincident with the true values of LiBr solution concentrations, but only sure that these true values ought to be included in the mentioned confidence intervals, if we have chosen the model suitably. Therefore, because we needed to substitute proper concentration values in the corresponding equations, we selected the mean values which would be close to the real ones. Therefore, the fact that some discrepancies appear in the mentioned sums does not imply that the measurements are inaccurate, but only implies that the choice of the LiBr solution concentration values is unsuitable.

The values of the *best* concentration presented in Table II, show that, with one exception, in the 60 wt % ethanol, all are included in the confidence intervals selected. This fact indicates that they have been properly chosen. Thus, in view of the previous assumptions, the transference numbers and concentrations that are closest to the real values are the *best* ones. Their values are shown in Table II and are the only ones used to calculate the different parameters here presented.

The behavior of the *best* transference numbers in all the ethanol–water mixtures, when the LiBr concentration changes, is similar to that shown by this parameter in aqueous solution (*2*). In Figure 1 we have plotted these cation *best* values against the square root of the *best* concentration for the different ethanol–water mixtures studied. In all cases the graph obtained is similar, although it can be seen that the points tend to move away from the limiting slope with the increase of ethanol in the mixture. This limiting slope was obtained in each mixture from the Stokes equation (*8*) by assuming the same behavior for LiBr in ethanol–water mixtures as in the aqueous

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

C, M	current, mA	$(T_+)_{obs}$	$(T_-)_{obs}$	$10^4\Delta T_{vol}$	$10^4\Delta T_{solv}$	$(T_+)_{cor}$	$(T_-)_{cor}$
X_{EtOH} = 0.042 (10%)							
$0.02068_8 \pm 0.0005_5$	1.50–1.75	0.3232_8		2.3	1.7	0.3232_2	
	0.61–0.74		0.6714_6	2.3	3.5		0.6720_4
$0.03033_1 \pm 0.0005_8$	1.82–2.22	0.3225_8		4.4	1.2	0.3222_6	
	0.93–1.33		0.6746_1	4.4	2.5		0.6753_0
$0.05248_0 \pm 0.0006_7$	3.53–3.99	0.3191_0		5.5	0.8	0.3186_2	
	1.53–1.80		0.6750_6	5.5	1.6		0.6757_7
$0.06671_0 \pm 0.0007_2$	3.84–4.48	0.3173_7		8.7	0.6	0.3165_6	
	2.66–2.72		0.6759_5	8.7	1.3		0.6779_5
$0.08581_6 \pm 0.0007_9$	4.56–4.96	0.3168_3		9.8	0.5	0.3159_0	
	2.84–3.21		0.6777_8	9.8	1.1		0.6788_7
X_{EtOH} = 0.089 (20%)							
$0.01697_3 \pm 0.0004_7$	0.90–1.31	0.3270_7		1.7	2.0	0.3271_0	
	0.63–0.70		0.6650_3	1.7	4.0		0.6656_0
$0.02586_7 \pm 0.0005_1$	1.36–1.66	0.3248_8		2.8	1.3	0.3247_7	
	0.81–1.15		0.6657_5	2.8	2.8		0.6663_0
$0.03317_5 \pm 0.0005_3$	2.16–2.42	0.3249_7		3.6	1.1	0.3247_2	
	1.38–1.41		0.6677_0	3.6	2.2		0.6682_8
$0.04381_0 \pm 0.0005_7$	3.02–3.21	0.3246_4		4.7	0.9	0.3242_6	
	1.94–1.98		0.6690_2	4.7	1.8		0.6696_6
$0.04734_0 \pm 0.0005_9$	3.41–3.64	0.3257_0		5.0	0.8	0.3252_8	
	1.93–2.27		0.6714_9	5.0	1.7		0.6721_5
$0.06071_9 \pm 0.0006_4$	4.32–4.73	0.3249_1		6.6	0.7	0.3243_2	
	2.82–3.06		0.6738_6	6.6	1.4		0.6746_5
X_{EtOH} = 0.21 (40%)							
$0.02634_9 \pm 0.0003_9$	0.80–0.89	0.3281_3		2.5	1.4	0.3280_2	
	0.95–1.16		0.6650_6	2.5	2.9		0.6656_0
$0.03299_3 \pm 0.0004_2$	1.09–1.41	0.3270_4		3.4	1.2	0.3268_2	
	1.21–1.42		0.6640_4	3.4	2.4		0.6646_2
$0.04861_9 \pm 0.0004_8$	1.70–1.91	0.3274_4		5.0	0.8	0.3270_2	
	1.94–2.20		0.6671_2	5.0	1.7		0.6678_0
$0.05352_9 \pm 0.0005_0$	1.91–2.11	0.3276_4		5.6	0.8	0.3271_6	
	1.95–2.31		0.6680_1	5.6	1.6		0.6687_3
$0.08607_7 \pm 0.0006_2$	2.97–3.15	0.3290_8		9.1	0.6	0.3282_3	
	3.21–3.61		0.6729_3	9.1	1.1		0.6749_5
X_{EtOH} = 0.37 (60%)							
$0.02041_0 \pm 0.0002_2$	0.46–0.50	0.3386_7		-1.6	2.7	0.3387_9	
	0.48–0.51		0.6586_2	1.6	5.3		0.6593_1
$0.02657_9 \pm 0.0002_4$	0.61–0.64	0.3460_5		-2.2	2.2	0.3460_5	
	0.58–0.62		0.6778_3	2.2	4.4		0.6784_9
$0.03626_9 \pm 0.0003_2$	0.96–1.01	0.3353_2		5.0	1.7	0.3349_9	
	0.83–0.87		0.6615_9	5.0	3.3		0.6624_2
$0.05254_1 \pm 0.0003_8$	0.98–1.20	0.3329_6		4.7	1.2	0.3326_1	
	1.06–1.40		0.6650_3	4.7	2.5		0.6657_5
$0.07025_8 \pm 0.0004_5$	1.05–1.30	0.3317_0		-8.6	1.0	0.3209_0	
	1.60–1.87		0.6693_8	8.6	2.0		0.6704_8
X_{EtOH} = 0.69 (85%)							
$0.02394_5 \pm 0.0001_1$	0.35–0.39	0.3681_8		-2.0	2.8	0.3682_6	
	0.43–0.47		0.6328_3	2.0	4.8		0.6335_1
$0.02875_3 \pm 0.0002_1$	0.38–0.43	0.3644_0		-2.1	2.4	0.3644_3	
	0.53–0.57		0.6338_7	2.1	4.2		0.6345_0
$0.03522_8 \pm 0.0002_1$	0.42–0.46	0.3636_7		-3.3	2.0	0.3635_4	
	0.66–0.70		0.6370_0	3.3	3.5		0.6376_9
$0.05135_2 \pm 0.0002_1$	0.59–0.63	0.3607_8		-5.9	1.5	0.3603_4	
	0.96–1.00		0.6420_5	5.9	2.7		0.6429_1
$0.05910_1 \pm 0.0002_1$	0.64–0.68	0.3600_5		-7.6	1.4	0.3594_3	
	0.95–0.99		0.6420_7	7.6	2.4		0.6430_7

solution for which that equation was evolved. The biggest separation from the limiting slope is reached in the mixture with 40 wt % ethanol, but afterward it narrows in the last two percentages of ethanol studied.

This behavior can be explained by considering some of the different effects that simultaneously act on the mobility of the solvated ions in a given ethanol–water solvent mixture. One is the increment in the viscosity of the medium caused by the increase of the LiBr solution concentration. This small increment must be relatively less as the absolute value of this viscosity increases. Another effect that can be considered is a structure-breaking and structure-making one. In fact, the structure-making capacity of the ions becomes less when the LiBr solution concentration increases along with the ion–ion interaction. This reduction in the structure-making capacity is greater in the case of the highly solvated Li^+ ions than in the case of Br^-. This situation leads to a relative decrease in the local viscosity around Li^+ ions with respect to the Br^- ions, which causes a relative increase in the mobility of the former. The change of the behavior in the ethanol-rich mixtures must be due to a viscosity effect as a result of the presence of ethanol molecules in the solvation sphere of the ions.

We now consider the effect of the ethanol content in the mixture on the limiting transference number values obtained. In Figure 2 the cation limiting values, T°_+, are plotted against the mole fraction of the cosolvent. As can be seen, the value of this transport parameter rises with the first additions of ethanol; afterward it tends to become flat and finally rises quickly

Table II. Summary of "Best" Cation Transference Numbers and "Best" Concentrations for LiBr in Ethanol-Water Mixtures at 25 °C

wt % EtOH	C, M	$\sum T_{cor}$	$(T_+)_{best}$	$10^4\Delta C$	C_{best}, M
10.0	$0.02068_8 \pm 0.0005_5$	0.9952_6	0.3247_6	0.9_8	0.02078_6
	$0.03033_1 \pm 0.0005_8$	0.9975_6	0.3230_5	0.7_3	0.03040_4
	$0.05248_0 \pm 0.0006_7$	0.9944_0	0.3204_2	2.9_5	0.05277_5
	$0.06671_0 \pm 0.0007_2$	0.9935_2	0.3186_3	4.3_5	0.06714_5
	$0.08581_6 \pm 0.0007_9$	0.9947_7	0.3175_6	4.5_0	0.08626_6
20.0	$0.01697_3 \pm 0.0004_7$	0.9927_0	0.3295_0	0.2_3	0.01699_6
	$0.02586_7 \pm 0.0005_1$	0.9910_4	0.3276_7	2.3_4	0.02610_1
	$0.03317_5 \pm 0.0005_3$	0.9930_0	0.3270_1	2.3_4	0.03340_9
	$0.04381_0 \pm 0.0005_7$	0.9939_2	0.3262_4	2.6_8	0.04407_8
	$0.04734_0 \pm 0.0005_9$	0.9974_4	0.3261_2	1.2_1	0.04746_1
	$0.06071_9 \pm 0.0006_4$	0.9999_7	0.3246_5	0.5_6	0.06077_5
40.0	$0.02634_9 \pm 0.0003_9$	0.9936_2	0.3301_3	1.6_9	0.02651_8
	0.03299_3 ● 0.0004_2	0.9914_3	0.3296_4	2.8_5	0.03327_8
	$0.04861_9 \pm 0.0004_8$	0.9948_2	0.3287_2	2.5_3	0.04887_2
	$0.05352_9 \pm 0.0005_0$	0.9958_9	0.3285_1	2.2_0	0.05374_9
	$0.08607_7 \pm 0.0006_2$	1.0021_8	0.3275_1	-1.8_3	0.08589_4
60.0	$0.02041_0 \pm 0.0002_2$	0.9981_0	0.3394_3	0.3_8	0.02044_8
	$0.02657_9 \pm 0.0002_4$	1.0245_4	0.3377_6	-6.3_7	0.02594_2*
	$0.03626_9 \pm 0.0003_2$	0.9974_1	0.3358_6	0.9_3	0.03636_2
	$0.05254_1 \pm 0.0003_8$	0.9983_6	0.3331_6	0.8_3	0.05262_4
	$0.07025_8 \pm 0.0004_5$	0.9913_8	0.3304_5	4.0_2	0.07066_0
85.0	$0.02394_5 \pm 0.0001_1$	1.0017_7	0.3676_1	-0.4_1	0.02390_4
	$0.02875_3 \pm 0.0002_1$	0.9989_2	0.3648_2	0.2_4	0.02877_7
	$0.03522_8 \pm 0.0002_1$	1.0012_3	0.3631_0	-0.4_1	0.03518_7
	$0.05135_2 \pm 0.0002_1$	1.0032_5	0.3591_8	-1.9_3	0.05115_9
	$0.05910_1 \pm 0.0002_1$	1.0025_0	0.3585_3	-1.4_6	0.05895_5

Table III. Summary of Limiting Cation Transference Numbers and Limiting Ionic Conductances for LiBr in Ethanol-Water Mixtures at 25 °C

wt % EtOH	T°_+	a, Å	$\lambda^\circ(Li^+)$, $ohm^{-1}\ cm^2\ equiv^{-1}$	$\lambda^\circ(Br^-)$,[a] $ohm^{-1}\ cm^2\ equiv^{-1}$
10.0	0.3356	4.1	27.9_8	55.4_0
20.0	0.3388	5.2	21.0_8	41.1_3
40.0	0.3428	5.5	14.8_7	28.5_1
60.0	0.3553	4.4	14.0_6	25.5_1
85.0	0.3900	5.1	15.4_7	24.1[b]

[a] From ref *5*. [b] From ref 7.

again when a great amount of ethanol is present. A first qualitative attempt to explain this relative increase of the lithium ionic mobility with respect to that of the bromide ions, as a consequence of the increasing presence of ethanol molecules in the medium, can, in general, be made by recurring to the variation that takes place in the solvation sphere of both lithium and bromide ions and the variation in the structure-modifying capacity of these ions. The former possibility is based on the assumption that a competition between the water dipoles and the cosolvent molecules takes place. This competition leads to a relaxation effect on the water molecules inside the ion solvation sphere which would weaken the dipole-ion interaction and ease the movement of the ion through the solution. This effect must be greater in the case of Li^+ ions than the Br^- ions due to the greater solvation capacity of the former, which explains the initial increase observed in Figure 2. However, the later increment of ethanol molecules in the medium must allow the entrace of these molecules into the ion solvation sphere, with the consequent increase of its size and therefore of the neutralization of the trend initially shown by its mobility. The last rise of this mobility, when the ethanol content in the mixture is very high, could be explained in terms of both a macroscopic viscosity effect of the solvent mixture and of a "sorting" effect (*5*), i.e., of the enrichment of water molecules in the solvation sphere of the ion with respect to the bulk solution mixture, which must be greater for Li^+ ions (of small size) than for Br^- ions (of a bigger size). This "sorting" effect would be more accentuated with the increase of the ethanol content of the mixture.

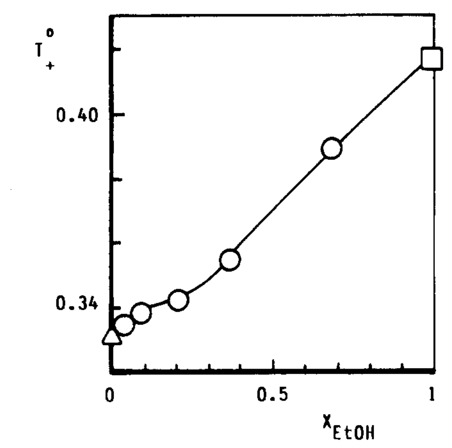

Figure 2. Effect of ethanol content on T°_+ values (○, this work; △, from ref *2*; □, from ref *7*).

In view of the previous comments, the structure-making capacity of the solvated Li^+ ions obviously diminishes markedly, or in other words the structure-breaking capacity increases greatly, with the rise in the ethanol content of the medium as a result of the desolvation that the ions undergo. At the same time, an increase in the structure-breaking capacity of the bromide ion must take place, but to a much smaller degree than for the lithium ion due to the less solvated state that the bromide ion presents.

The values found for the *a* parameter by the use of the Fuoss and Onsager equation which are shown in Table III are rather large (between 4.0 and 5.5 Å) when compared with those obtained by conductance measurements in this laboratory for other alkali-metal halides in the same ethanol-water mixtures (*9*, *10*), especially if we take into account that in these ethanol-water mixtures no ionic association was detected. Nevertheless, the extrapolated T° values thus found are good enough to be accepted.

Finally a short comment is necessary about the limiting conductances obtained. Those here presented show differences when compared with the values previously reported in the literature (*5*), which become large at high ethanol content in the mixture (approximately 2 and 5 $ohm^{-1}\ cm^2\ equiv^{-1}$, for 60 and 85 wt % ethanol, respectively). Nevertheless, both series of data present a similar behavior with the increase of the ethanol content, and therefore, such discrepancies must be due to small errors involved in the procedure used to obtain the conductance values.

By looking at these conductance values, collected in Table III, it can easily be seen that there is a more pronounced decrease for the Br^- ions, with the first additions of ethanol, than for the Li^+ ions. This different effect of the ethanol content on the mobility of both types of ions explains the initial steep rise, previously indicated, for the Li^+ ions when Figure 2 was analyzed. As the medium becomes richer in ethanol, the participation of the two different ionic species, Li^+ and Br^-, in the transport of the electrical charge throughout the solution, tends to be equal; i.e., it looks as if the ethanol exerts a leveling effect on the mobilities of both types of ions.

Registry No. LiBr, 7550-35-8; Li, 7439-93-2; Br^-, 24959-67-9.

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Vapor–Liquid Equilibrium in Binary Systems of Chlorotrifluoromethane with *n*-Butane and Isobutane

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Vapor and liquid equilibrium phase compositions were determined at 310.93, 350.00, and 400.00 K for the binary systems of chlorotrifluoromethane (R 13) with *n*-butane and with isobutane. The data were fit with the Peng–Robinson equation of state. Henry's constants were derived, and their temperature behavior is compared with a new model calculation.

Introduction

Chlorotrifluoromethane (R 13) is used as a refrigerant in low-temperature specialty situations such as cooling brine solutions, in the lower stage of cascade refrigeration systems, and also in an azeotropic mixture with CHF_3 (R 23) in very low temperature cascade systems. At present it is the only fully halogenated alkane whose future use has not been limited by international agreement (*1*).

Densities and vapor pressures of pure R 13 have been measured by several workers (*2–6*), and several reports exist for the measurement of the densities and vapor–liquid equilibrium properties for R 13 in mixed refrigerant systems, generally with R 12, R 14, and R 23 (*7–12*). As far as we are aware, however, the present measurements are the first that have been reported on mixtures of R 13 with hydrocarbons at elevated temperatures and pressures.

This work is a continuation of our vapor–liquid equilibrium measurements on systems involving one supercritical component. These systems are binary mixtures of a small quasi-spherical molecule, R 13, which has a moderate dipole moment (0.5 D) with the two isomers of a larger nonspherical molecule, butane, which have very small dipole moments ($\leq$0.05 and 0.13 D).

In the next section we give a brief description of the apparatus and then a summary of the experimental results. In the final section we compare our experimental results with a new model for correlating Henry's constant and the partition constant *K* at infinite dilution near the solvent's critical point.

Experimental Section

The apparatus has been described previously (*13*), and only a brief description will be given here. The VLE cell is a heavy-wall vessel (volume approximately 65 cm^3) which is made of 300 series stainless steel and which has a window in one side. Vapor is circulated from the top of the vessel and bubbled through the liquid phase in the bottom by means of a magnetically driven pump. The liquid phase is also circulated via a high-pressure dual piston pump. The system pressure is measured in the liquid circulation line with two digital bourdon gauges having pressure ranges 0–34 and 0–138 bar. Temperature is measured with a probe-type platinum resistance thermometer inserted into the top of the VLE cell. With the exception of the pressure gauges, liquid circulation pump, and the vapor circulation pump motor, the apparatus is mounted inside a convection oven. The oven has a window for visual observations. Rotating sampling valves in the circulation lines allowed small samples of each phase to be analyzed with a gas chromatograph and electronic integrator.

The thermometer and ac bridge had an overall accuracy of ±0.025 K and a sensitivity of better than 0.005 K. The calibration was checked at the triple point of water. The air temperature in the oven had a short-term oscillation of ±0.03 K, and the average temperature could be set and repeated to within about 0.01 K. The temperature homogeneity in the workspace was measured to be about ±0.025 K at 340 K. The pressure gauges were calibrated periodically against laboratory standards, and their accuracy was estimated to be ±0.03 bar.

The relative response factors of the chromatograph for each of the three components were found by using pure samples covering the size range encountered experimentally. For isobutane and *n*-butane they were constant and had relative values of 1.550 and 1.554, respectively. For R 13, however, the factor varied linearly with the area of the peak and had a value of $1.618 + 0.01202A$, where *A* is proportional to the peak area. In this work *A* varied from 0 to 20 with the largest values occurring in the vapor phase at the highest pressures and highest R 13 concentrations. The response factors could be determined with a standard deviation of 0.25%, and with the normalizing action of the integrator we estimate the compositions to have an uncertainty given by $|\delta x| = 0.005x_1x_2 + 0.0003$ and $|\delta y| = K_1K_2|\delta x|$ in mole fraction (where $K_i = y_i/x_i$).

The butane samples came from several cylinders having purity levels varying from 99.94 to 99.99 mol%. The R 13 cylinder was certified as having a minimum purity of 99%. In fact, we found that it had a volatile impurity of 0.1%, which appeared to be air. After several samples were taken this impurity dropped to about 0.04%. No other impurities were found with the chromatograph.

Data were measured on isotherms, and each run began with a determination of the vapor pressure of the pure butane. After that successive increments of R 13 were added and the vapor and liquid circulation pumps were run until equilibrium was es-