

KINETICS AND MECHANISM OF DEHYDRATION OF ISOPROPYL AND *sec*-BUTYL ALCOHOLS
ON CATALYSTS CONSISTING OF QUARTZ COATED BY LIQUID PHOSPHORIC ACID
AND MIXTURES OF PHOSPHORIC ACID AND KH_2PO_4

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UDC 541.127:541.128:542.936

In continuation of the study [1, 2] of the kinetics of dehydration of aliphatic alcohols in the presence of a phosphoric acid catalyst, we have investigated the dehydration of isopropyl alcohol (IPA) [3]; the objective was to check the procedure based on pulsed chromatography, to establish more precisely the mechanism of this reaction, and also to obtain improved experimental data on the kinetics of dehydration of *sec*-butyl alcohol.

EXPERIMENTAL

The pulsed chromatographic procedure has been described in [1, 2]. The sample volume introduced into the reactor was 0.5 μl iter. The reactor was a quartz tube 90 mm long, with an internal diameter of 12 mm. The particle size of the support was 0.5-1 mm. The H_3PO_4 concentration in the liquid phase of the catalyst without the addition of salts was determined from the equilibrium vapor tension of water vapor pH_2O . For this purpose we have used the data in [4, 5] to calculate the pH_2O of aqueous solutions with different concentrations of H_3PO_4 for the temperatures of the kinetic experiments by extrapolation of $\log \text{pH}_2\text{O}$ as a function of $1/T$.

In the investigated range of compositions of the acid solutions we have found an empirical relationship between $\log \text{pH}_2\text{O}$ and the logarithm of the molar $\text{H}_2\text{O}:\text{H}_3\text{PO}_4$ ratio; this relationship was used to determine the H_3PO_4 concentration in the liquid phase for a given value for pH_2O . The catalyst without KH_2PO_4 was prepared by the procedure given in [2] and the H_3PO_4 content determined according to [6].

In the tests involving the addition of salts the quartz was coated with an aqueous H_3PO_4 solution containing from 7.04 to 58.8 mole % KH_2PO_4 (with respect to H_3PO_4). The quartz with the solution applied was heated to 330°C; after the treatment at high temperature the catalyst was packed into the reactor and kept in a H_2O atmosphere with a given pH_2O . A constant rate constant of the investigated reaction served as the criterion that the given composition of the liquid phase of the catalyst had been reached, i.e., that the equilibrium between liquid and vapor had been established. When the kinetic experiments were completed, the acid and salt were removed from the quartz by refluxing and the obtained solution analyzed for its acid content and K^+ by atomic absorption spectrometry.

The retention volume V_R was determined as the difference between the products of the carrier gas flow rate and the time required for the appearance of the alcohol peak in tests carried out at the same temperature pH_2O with two equal reactors and carriers, whereby the carrier in one of the reactors was coated with H_3PO_4 . In order to determine V_R , kinetic tests were carried out at a flow rate at which the error in the degree of conversion of the alcohol was the smallest. The functions of the acidity H_0 of the aqueous H_3PO_4 solutions for 90 and 110°C were obtained by extrapolation from the linear relationship of H_0 from $1/T$ by using the data for 24°C [7] and 70°C [8]; the latter data were corrected for changes in the pK_{BH^+} of the indicators with temperature, used to measure the acidity of H_3PO_4 .

The value of pK_{BH^+} for *o*-nitroaniline at 70°C is equal to -0.48 [9] and 0.59 [10]; we have used the value -0.48 to calculate H_0 at 70°C. The pK_{BH^+} values of the other indicators (Table 1 and 2) have been obtained using the usual method.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 10, pp. 2195-2201, October, 1986. Original article submitted January 25, 1985.

TABLE 1. Kinetics of Dehydration of Isopropyl Alcohol at 110 °C on a Catalyst Consisting of Quartz Coated with 124.2 mg H₃PO₄. Carrier Volume 3.1 ml

Parameter	H ₃ PO ₄ , %				
	79,2	86,1	91,7	94,7	97,2 *
lg p _{H₂O}	2,46	2,17	1,82	1,50	1,124
lg a _{H₃PO₄}	+0,39	+0,70	+0,94	+1,07	+1,16
H ₀	-2,34	-2,77	-3,11	-3,30	-3,51
lg k _l	-0,92	-0,57	0	+0,27	+0,55
lg k _l /h ₀	-3,26	-3,34	-3,11	-3,03	-2,96
lg k _l /a ² _{H₃PO₄}	-1,70	-1,97	-1,88	-1,87	-1,77
k _{eff} , ml/min	0,90	4,6	25,0	61,2	42,0
V _R , ml	7,5	16,8	25,2	32,7	11,8

TABLE 2. Values of k_{eff}, k_l, and V_R for the Dehydration of Isopropanol at Different Temperatures on a Catalyst Containing 86.1% H₃PO₄ in the Liquid Phase (H₃PO₄ 124.2 mg; carrier volume 3.1 ml)

Parameter	T., °C			
	90	100	110	120
PH ₂ O, torr	66	100	148	224
k _{eff} , ml/min	1,7	2,7	4,6	8,0
V _R , ml	39,0	26,2	16,8	11,3
k _l , min ⁻¹	0,043	0,1	0,27	0,71

RESULTS AND DISCUSSION

The kinetic curves of the dehydration of IPA obtained at constant p_{H₂O} are described by the equation

$$k_{\text{eff}} = w \ln n_0/n_i \quad (1)$$

where n₀ and n_i are the initial and the current amounts of the alcohol; k_{eff} is the effective rate constant of dehydration; w is the carrier gas flow rate which was varied from 4 to 60 ml/min. The reaction takes place in the kinetic region [11]. The average of 4-5 measurements was taken at every value of w. Equation (1) describes satisfactorily the kinetic curves from 10 to 90% dehydration of the alcohol.

In order to obtain the rate constants of the dehydration in the liquid phase k_l we have measured the retention volume V_R; k_l was then calculated from the equation

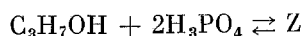
$$k_{\text{eff}} = k_l V_R \quad (2)$$

The activities of the phosphoric acid a_{H₃PO₄} were calculated from the equations of Gibbs and Duhem; the values of a_{H₂O} were taken from [5, 6]. A 70 mass % solution was taken as the standard solution (a_{H₃PO₄} = 1). It follows from Table 1 that there is no linear correlation between log k_l and H₀ in the case of dehydration in the absence of KH₂PO₄; instead, the following correlation holds:

$$\lg k_l - 2 \lg a_{\text{H}_3\text{PO}_4} = \text{const} \quad (3)$$

The data on the protonation constants of aliphatic alcohols are conflicting. The basicity constants of IPA [12-14] have been obtained on the basis of kinetic measurements taken in reactions with the participation of the alcohol, assuming that protonation of the alcohol is one of the factors representing the influence of the medium on the rate constant of the investigated reaction (k_{eff}). However, when deriving the equation for k_{eff} as function of the acidity of the solution, assumptions have been made, which are not entirely justifiable, about the influence of the medium on the factor with the activity coefficients in the equation representing k_{eff} as function of the parameters of the medium.

Equation (3) can be interpreted by making the following assumptions: under the conditions at which the kinetic tests have been performed in the present work, IPA is practically not ionized; the complex Z, which can react in the dehydration, is formed from the nonionized form of the alcohol and two molecules of H_3PO_4



The relative concentration of such complexes is small, so that it can be neglected in the material balance with respect to the alcohol: in the limiting stage the complex Z decomposes into the reaction products. In order to obtain the equation which describes the influence of the medium on k_l , we must express the equilibrium constant for the formation of complex Z through parameters that characterize the properties of the medium

$$\frac{a_{C_3H_7OH} a_{H_3PO_4}^2}{a_Z} = K_Z$$

By expressing the activity of the alcohol and of the complex through the concentrations and activity coefficients, we obtain for CZ

$$C_Z = \frac{C_{C_3H_7OH} a_{H_3PO_4}^2}{K_Z} \frac{f_{C_3H_7OH}}{f_Z}$$

When the composition and charge of complex Z and of the activated dehydration complex are the same, we can assume that their activity coefficients (f_Z and f^*) change in the same way when the composition of the medium is varied. In this case, the following equations are valid for the influence of the medium on the reaction rate W and the liquid-phase rate constant k_l :

$$W = k \frac{a^*}{f^*} = k_{or} \frac{a_Z}{f_Z} = \frac{k_{or}}{K_Z} C_{C_3H_7OH} a_{H_3PO_4}^2 \frac{f_{C_3H_7OH}}{f_Z} \quad (4)$$

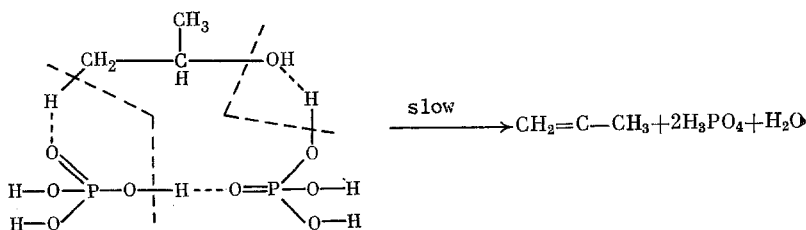
$$k_l = \frac{k_{or}}{K_Z} a_{H_3PO_4}^2 \frac{f_{C_3H_7OH}}{f_Z}$$

According to experimental data, $k_l/a_{H_3PO_4}^2 \approx \text{const}$ within the limits of experimental error; this is possible under the condition that the factor $f_{C_3H_7OH}/f_Z$ in (4) is independent of the composition of the medium.

In such a case we have

$$k_l/a_{H_3PO_4}^2 = k_{or}/K_Z$$

The conversion of Z to reaction products is expressed schematically as follows



The experiments with IPA were performed in highly concentrated solutions of H_3PO_4 where a_{H_2O} is small. It can be assumed that in the dehydration of alcohols the H_2O molecule can act in more dilute acid solutions as an H^+ acceptor of the C-H bond. In this case the rate constant will be proportional to the product $a_{H_3PO_4} a_{H_2O}$, when the factor with the ratio of the activity coefficients of the nonionized alcohol and the reactive complex is independent of the composition of the medium. In order to verify whether the formation of such a complex is possible, we must study the dehydration of an alcohol with a high reactivity. The participation of the monohydrates $H_3PO_4 \cdot H_2O$ and $HClO_4 \cdot H_2O$ in the limiting stage of the dehydration of alcohols has been established on the conversion of the equilibrium mixture of dimethylvinyl carbinol and dimethylallyl alcohol to isoprene [15]. In this reaction, the catalytic effect is attributed to the ability of hydrates of strong acids (which represent ion pairs) to form donor-acceptor complexes, due to coordination of H_3O^+ and the OH group of alcohol and the anion with the H atom of the C-H bond. It is possible that in the investigated reactions two molecules of H_3PO_4 manifest the properties of the ion pair $H_4PO_4^+ \cdot H_2PO_4^-$

TABLE 3. Kinetics of Dehydration of sec-Butanol at 90°C on a Catalyst Consisting of Quartz Coated with 34.5 mg H₃PO₄ (volume of weight taken 1.1 ml)

Parameter	H ₃ PO ₄ , %						
	77,83	81,20	82,57	85,35	87,56	91,27	93,54
log p _{H₂O}	2.12	2.0	1.95	1.82	1.70	1.45	1.25
log α _{H₃PO₄}	0.41	0.57	0.63	0.76	0.88	1.04	1.13
H ₀	-2.42	-2.63	-2.70	-2.90	-3.03	-3.22	-3.41
log k _ℓ	-1.04	-0.82	-0.68	-0.47	-0.19	+0.03	+0.31
log k _ℓ / η ₀	-3.46	-3.45	-3.38	-3.37	-3.22	-3.19	-3.10
log k _ℓ / a ² H ₃ PO ₄	-1.86	-1.96	-1.94	-1.99	-1.95	-2.05	-1.95
k _{eff} , ml/min	0.7	1.6	2.5	7.5	15.9	33.1	64.0

TABLE 4. Effect of KH₂PO₄ on the Catalytic Activity of Phosphoric Acid in the Dehydration of Isopropyl Alcohol (110°, p_{H₂O} = 31.6 torr*)

Parameter	Catalyst volume, ml				
	3.1	3.0	3.1	3.0	3.2
H ₃ PO ₄ mass, mg	124.2	137.2	124.2	84.2	9.7
KH ₂ PO ₄ mass, mg	0	14.5	38.2	55.4	19.7
M _{salt} / M _{H₃PO₄} †	0	0.076	0.22	0.47	1.46
k _{eff} , ml/min	61.2	27.5	3.03	0.12	0.08
V _R , ml	32.7	35.8	15.4	5.2	≈1.0
k _ℓ , min ⁻¹	1.9	0.8	0.2	0.04	≈0.08
$\frac{k_{\ell}(M_{H_3PO_4} + M_{KH_2PO_4})}{M_{H_3PO_4}}$ min ⁻¹ · mole ⁻¹	1.9	0.88	0.28	0.07	≈0.24

*Such an equilibrium water vapor tension is obtained with 94.7% H₃PO₄ in water at 110°C.

†M_{salt} and M_{H₃PO₄} are the amounts of salt and acid in mole, respectively.

The values of k_ℓ and k_{eff} (min⁻¹), obtained in the interval for 90-120°C for 86.07% H₃PO₄, fit well on the straight lines in the Arrhenius coordinates

$$\lg k_{\ell} = -6,00 \cdot 10^3 / T + 15,09$$

$$\lg k_{\text{eff}} = -3,38 \cdot 10^3 / T + 9,51$$

As expected, log V_R is a linear function of 1/T: log V_R = (2.67 · 10³/T) - 5.76 (in the range 90-120°). The enthalpy of dissolution of IPA in 86.07% H₃PO₄ is equal to 51.2 kJ/mole. The activation energy of dehydration of IPA in the liquid acid E_ℓ = 114.9 kJ/mole, the temperature function of k_{eff} is determined by E_{eff} = 64.8 kJ/mole.

In 84.5% H₃PO₄ at 117.5°C, log k_ℓ = -0.35 (k_ℓ in min⁻¹) [3]. It follows from the present work that at 110°C, log k_ℓ / H₃PO₄² = -1.86 ± 0.15. Based on the value of α_{H₃PO₄} for 84.5% H₃PO₄ at 110°C, log k_ℓ = -0.58 ± 0.15. It can be assumed logically that E_ℓ remains unchanged when the acid concentration changes by 1.6%. By using the value E_ℓ = 114.9 kJ/mole we obtain for 84.5% H₃PO₄ at 117.5°C, log k_ℓ = -0.28 ± 0.15; this agrees with the results obtained in [3]. Consequently, the data for the phosphoric-acid catalyst prepared by the procedure given in [1], obtained by pulsed chromatography, are correct.

Errors exist in the H₃PO₄ concentrations and the values of H₀ at 90°C, due to the fact that the change of the pK_{BH⁺} of the indicators used to measure the acidity of the medium with temperature has not been taken into account. In our case this leads to large errors because H₀ at elevated temperatures was obtained by extrapolation from two points: 24 and 70°C. The H₃PO₄ concentration in the liquid phase of the catalyst was determined from the equilibrium values of p_{H₂O}; however, it was found that the empirical equation given in [2] for p_{H₂O} as function of the molar ratio H₂O:H₃PO₄, based on the data from [4, 5], describes in-

TABLE 5. Influence of Equilibrium Water-Vapor Tension on the Catalytic Activity in the Dehydration of Isopropanol of a Catalyst Consisting of Quartz Coated with 137.2 mg H₃PO₄ and 14.5 mg KH₂PO₄ (volume of support 3.0 ml; 110°C)

Parameter	p _{H₂O} , torr				
	31,6	66	117	148	195
k _{eff} , ml/min	27.5	17.5	6.2	3.7	1.9
V _R , ml	35.8	29.4	22.3	17.9	13.4
k _ℓ , min ⁻¹	0.77	0.60	0.28	0.21	0.14

TABLE 6. Influence of Temperature on the Catalytic Activity of a Catalyst Consisting of Quartz Coated with 137.2 mg H₃PO₄ and 14.5 mg KH₂PO₄, at Equilibrium Water-Vapor Tensions Corresponding to 91.70% H₃PO₄, in the Dehydration of Isopropyl Alcohol (volume of support 3.0 ml)

Parameter	T, °C			
	110	120	130	140
p _{H₂O} , torr	66	105	132	224
k _{eff} , ml/min	17.5	28.0	36.0	52.5
V _R , ml	29.4	20.8	14.9	9.7
k _ℓ , min ⁻¹	0.60	1.35	2.42	5.41

correctly this relationship. Correct results are obtained by using the correlation between p_{H₂O} and the molar ratio H₂O:H₃PO₄, derived in the present work.

We have checked the values of k_ℓ of sec-butanol (SB) in solutions at p_{H₂O} = 132 and 18 torr at 90°C (77.83 and 93.54% H₃PO₄, respectively). Under such conditions the rate constants are obtained at the extreme carrier gas flow rates obtainable with our equipment (the lowest with 77.83% H₃PO₄ and the highest with 93.54%).

In the experiments with p_{H₂O} = 132 torr the value of k_ℓ for SB was found to be the same as in [2], while in the experiments with p_{H₂O} = 18 torr, log k_ℓ = 0.32, not 0.49 as given in [2].

With account taken of the above corrections, k_ℓ for SB correlate better with α_{H₃PO₄}² than with H₀. At 90° for this alcohol, log k_ℓ/α_{H₃PO₄}² = -1.96 ± 0.1. The reactivities (k_{or}/K_Z) for SB and IPA can be compared by comparing log k_ℓ/α_{H₃PO₄}² of these alcohols at 90°C. The value obtained for IPA in 86.07% H₃PO₄ at 90° was log k_ℓ = -1.36. The temperature function at 90°C gives log k_ℓ = -1.41; consequently, log k_ℓ/α_{H₃PO₄}² = -2.93 ± 0.03. Thus, in 86.07% H₃PO₄ at 90°C the reactivity of SB is higher by one order of magnitude than that of IPA (Table 3).

A reactive complex may be formed from the nonprotonated alcohol and a molecule of pyrophosphoric acid under the condition that the alcohol is protonated to a significant degree. In this case, the influence of the medium on k_ℓ must be expressed by the equation

$$k_{\ell} = \frac{(k_{or}/K_Z) \alpha_{H_3PO_4}^2 / \alpha_{H_2O}}{1 + h_0/K_Z}$$

The kinetic data for IPA are not described by this equation when using the values of H₀ calculated at 110°C; the equation is valid for SB at 90°C but gives a low basicity constant.

The influence of KH₂PO₄ added on the catalytic activity of H₃PO₄ applied on quartz was studied at 110°C and different equilibrium values of p_{H₂O}. At a given initial salt:acid ratio the catalytic activity of the solution depends on the equilibrium p_{H₂O}. At constant p_{H₂O} the rate constants k_{eff} and k_ℓ decrease with increasing salt/H₃PO₄ ratio (molar) in solution (Table 4). At the same time, k_ℓ (MH₃PO₄ + MKH₂PO₄)/MH₃PO₄, a constant referred to 1 mole H₃PO₄ in the liquid phase of the catalyst, drops only to MKH₂PO₄/MH₃PO₄ = 0.47; for a catalyst

with $\text{MKH}_2\text{PO}_4/\text{MH}_3\text{PO}_4 = 1.46$ it is commensurate with the value for the mixture with $\text{MKH}_2\text{PO}_4/\text{MH}_3\text{PO}_4 = 0.076$. The obtained value of $k_\ell (\text{MH}_3\text{PO}_4 + \text{MKH}_2\text{PO}_4)/\text{MH}_3\text{PO}_4$ for the catalyst with the highest molar salt concentration exceeds significantly the experimental error. Consequently, the increase in $k_\ell (\text{MH}_3\text{PO}_4 + \text{MKH}_2\text{PO}_4)/\text{MH}_3\text{PO}_4$ can be attributed to the catalytic effect of the salt itself as an aprotic acid. It is expedient to study this effect more closely.

At a constant temperature the increase in pH_2O above a catalyst coated with given amounts of salt and H_3PO_4 leads to a decrease in $k_{\text{eff}} \cdot V_R$, and k_ℓ , whereby $\log V_T$ increases linearly with increasing pH_2O (Table 5): $\log V_R = 1.65 - 2.67 \cdot 10^{-3} \text{pH}_2\text{O}$.

In order to determine quantitatively the influence of the addition of KH_2PO_4 and H_3PO_4 at different temperatures [16], we have investigated the dehydration of IPA on a catalyst containing H_3PO_4 and KH_2PO_4 and equilibrium vapor tensions pH_2O , corresponding to the same concentration of H_3PO_4 in mixtures with H_2O (Table 6). As expected, k_ℓ and k_{eff} increase while V_R decreases with increasing temperature: $\log V_R = 2.57 \cdot 10^3/T - 5.19$; $\log k_\ell = -5.17 \cdot 10^3/T + 13.12$; $\log k_{\text{eff}} = -2.58 \cdot 10^3/T + 7.97$.

In the catalyst coated with 137.2 mg H_3PO_4 and 14.5 mg KH_2PO_4 with a pH_2O corresponding to 91.7% H_3PO_4 in water, the dissolution enthalpy of IPA is 49.2 kJ/mole. The activation energy for k_ℓ is equal to 99.0 kJ/mole, for k_{eff} it is equal to 49.4 kJ/mole. The temperature function of k_ℓ in 86.07% H_3PO_4 (see above) gives $E_\ell = 114.9$ kJ/mole. There is no reason to expect a significant difference in E_ℓ for the reaction in 91.7% H_3PO_4 . On the catalyst containing KH_2PO_4 and at a pH_2O corresponding to 91.7% H_3PO_4 in a solution free of salt, E_ℓ is smaller by 24 kJ/mole. Consequently, the inhibiting effect of salt increases with temperature.

The authors wish to express their gratitude to A. A. Levshina, T. B. Epshtein, and V. A. Bessonov (NIUIF) for the determination of the K^+ contents.

CONCLUSIONS

1. A pulsed chromatographic method was used to investigate the kinetics and mechanism of dehydration of isopropyl alcohol on catalysts consisting of fused quartz coated with phosphoric acid and phosphoric acid with potassium dihydrophosphate.
2. Data on the dehydration of sec-butanol on a catalyst consisting of quartz coated with phosphoric acid have been checked and their precision improved.
3. In the experiments with catalysts without the addition of salt, the rate constant of the dehydration of secondary propyl and butyl alcohols increases proportionally to the square of the thermodynamic activity of the acid when the concentration of the phosphoric acid in the liquid phase is changed. This fact is attributed to the participation of the nonionized alcohol molecule and two molecules of phosphoric acid in the limiting stage of the reaction.

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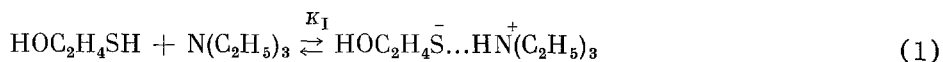
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STUDY OF SOME PHYSICOCHEMICAL PROPERTIES OF THE β -HYDROXYETHYL
 MERCAPTAN-TRIETHYLAMINE SYSTEM AND CALCULATION OF THE CONCENTRATION
 OF IONS AT 15-45°C

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UDC 537.311:547.269.1:547.233.3

Hydroxyalkyl sulfides, used in the synthesis of stabilizers for polyolefins, are prepared according to a reaction in which the olefin oxide reacts with the mercaptid ion generated by the β -hydroxyethyl mercaptan-triethylamine system (HEM-TEA) in one of the stages [1, 2]. The conductivity, viscosity, density, and dielectric constant of HEM, TEA, and their mixtures were measured for several temperatures, and the values of the concentrations of mercaptid ions which appear in the following reactions were calculated based on them:



EXPERIMENTAL

Triethylamine was purified according to [3] and β -hydroxyethyl mercaptan was purified according to [4]. The conductivity of the HEM-TEA system was measured in the range of 54-100 mole % HEM using a 5300 V Conductolyser. The conductivity of the samples of HEM-TEA mixtures (Tables 1 and 2 and Fig. 1a) prepared by suspension was measured at 15, 35, and 45°C ($\pm 0.1^\circ\text{C}$) as in [1]. The error in measurement of the conductivity did not exceed 1%. The viscosity of the starting HEM, TEA, and their mixtures (Figs. 1b and 2) was determined at 15, 35, and 45°C ($\pm 0.1^\circ\text{C}$) using an Ostwald viscosimeter, and the precision of measurement was 0.5%. In determining the cell constant, water, benzene, and CCl_4 were used as the calibration liquids. The density (Fig. 3) was determined pycnometrically for the 0-100 mole % HEM range at 35 and 45°C ($\pm 0.1^\circ\text{C}$), and the error of measurement was $(2-3) \cdot 10^{-4}$ g/cm³. The density for 15 and 25°C is given in [2, 5]. The dielectric constant (Table 3) was determined in the range of 0-50 and for 100 mole % HEM at 35 and 45°C ($\pm 0.1^\circ\text{C}$) with an OH-301 G. Sabot system universal dielectrometer at a frequency of 3 MHz. Benzene, MeOH, and acetone were used as the calibration liquids. The error in determining the dielectric constant did not exceed 1-2%. The value of the dielectric constant of HEM, TEA, and their mixtures at 15 and 25°C were taken from [2, 5].

RESULTS AND DISCUSSION

As Fig. 1a shows, the maximum of the specific conductivity of the HEM-TEA system occurs at 90-95 mole % HEM. The maximum viscosity (cf. Fig. 1b) occurs at 93-95 mole % HEM. Similar dependences of the specific conductivity and viscosity were obtained for 35 and 45°C. For calculating the concentrations of ions in the HEM-TEA system, the values of the concentration of the ion pair CI for 15°C for the 50-100 mole % HEM range were obtained from spectroscopic studies of the HEM-TEA system [5]. The values of the concentrations of the ion pair for 35 and 45°C were calculated for a narrow (98-100 mole % HEM) range of concentrations of TEA in HEM based on the results in [2, 5]. According to the data from Raman spectroscopy for 15 and 25°C, equilibrium (1) in the 85-100 mole % HEM range is shifted to the right and all

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 10, pp. 2201-2206, October, 1986. Original article submitted March 14, 1985.