Keto-Enol Tautomerism and the Dipole Moment of the Association in the Cyclohexanone + Carbon Tetrachloride Mixture

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Summary. A measuring method and an apparatus have been developed for the determination of the dipole moment of the keto-enol association complex formed in cyclohexanone and in its mixtures. It was stated that both the dipole moment and the amount of the association can be determined by the measurement of the static relative permittivity and the Piekara constant in mixtures of cyclohexanone with nonpolar components. It was found that the association is practically nonpolar $[\bar{\mu} = 1.18 \cdot 10^{-30}\,Cm\ (0.35\,D)]$, and the enol formation in the ketone increases with the amount of the diluting nonpolar component. The modelling of the mixture was also made in the form of an $A + A_2 + B$ type ternary mixture using the vapour-liquid equilibrium data of the cyclohexanone + carbon tetrachloride mixture. The degree of enol formation was calculated on the basis of the excess Gibbs free energy of mixing and the static relative permittivity. It was found that the results obtained exclusively from dielectric data (ε and λ) show a good agreement with those calculated from the thermodynamic model.

Keywords. Keto-enol tautomerism; Association; Static relative permittivity; Piekara-constant; Vapour-liquid equilibrium.

Keto-Enol-Tautomerie und das Dipolmoment des Assoziats im Cyclohexanon-Tetrachlorkohlenstoff-Gemisch

Zusammenfassung. Es wurde eine Meßmethode und ein Gerät zur Bestimmung des Dipolmoments des Assoziationskomplexes des sich in Cyclohexanon und dessen Gemischen bildenden Keto-Enols ausgearbeitet. Es wurde festgestellt, daß durch das Messen der statischen relativen Dielektrizitäts- und Piekara-Konstanten sowohl das Dipolmoment des Assoziats, als auch dessen Menge in den Gemischen des Cyclohexanons mit apolaren Komponenten bestimmt werden können. Man stellte fest, daß das Assoziat praktisch apolar ist $[\bar{\mu} = 1.18 \cdot 10^{-30}\,Cm\ (0.35\,D)]$, und daß sich die Enolisation im Keton durch Verdünnung mit den apolaren Komponenten erhöht. Die Dampf-Flüssigkeit-Gleichgewichtsdaten des Cyclohexanon-Tetrachlorkohlenstoff-Gemisches wurden berücksichtigt und das Gemisch auch als ein Ternärgemisch $A + A_2 + B$ modelliert; so konnte die Enolisation aufgrund des Überschusses der Freien Enthalpie bei der Vermischung und der statischen relativen Dielektrizitätskonstante berechnet werden. Es wurde festgestellt, daß die aus den dielektrischen Daten berechneten Resultate gut mit den aufgrund des thermodynamischen Modells berechneten Resultaten übereinstimmen.

Introduction

The dissimilarity of cyclohexanone to common aliphatic monoketones is that — in addition to its other special properties — it contains much more enol forms than other ketones in pure liquid state at temperatures close to the ambient (approximately in the 0 to 80 °C range).

While the enol content of aliphatic monoketones is in the order of 10^{-4} to $10^{-1}\%$, the classical enol form in cyclohexanone at temperatures of 293.15 K and 313.15 K is 1.2% (determined by titration) and 1.7% (determined by IR spectroscopy), respectively [1, 2].

It was pointed out in previous papers [3] that the keto-enol equilibrium of ketones in their mixtures with nonpolar, or less polar components is significantly shifted toward the direction of enol formation. Therefore, it can explain the fact that the gas chromatographic determination of cyclohexanone is practically impossible, since the enol form present gives a separate peak in the chromatogram. Since the amount of the enol form depends — to a certain extent — on the history of the sample, its presence in the sample disturbs the quantitative evaluation of the chromatogram, as well [3].

The relatively high enol content of cyclohexanone offers an excellent possibility for the study of the equilibrium of keto-enol tautomerism as well as the properties and the formation of keto-enol associations. Thus, the goal of this work was to obtain information on the phenomena mentioned and on the properties of the real components through the study of the cyclohexanone — carbon tetrachloride mixture. For this purpose — beside the thermodynamic characteristics of mixing — the dielectric properties (static relative permittivity and the Piekara constant) were measured.

Experimental

Measurements were carried out at 293.15 ± 0.05 and 313.15 ± 0.05 K. Density (ρ) was measured by means of an Anton Paar digital densimeter type DMA 02 C, while refractive indices (n_D) were determined by an Abbé refractometer. Static relative permittivity (ε) was measured at a frequency of 1 MHz by a Siemens impedance bridge (Rel. 3. 277 a). The Piekara constant (λ) was determined by an apparatus designed in our laboratory (discussed later), while vapour-liquid equilibrium data from which the excess Gibbs free energy of mixing (G^E) was calculated were obtained by means of a dynamic device similar to that of Stage et al. [4].

Analytical grade cyclohexanone and carbon tetrachloride were supplied by Reanal. The materials were further purified by dehydration and rectification according to recommendations described in the literature [5]. The pure compounds were tested by gas chromatography.

An Apparatus for the Determination of the Piekara Constant

The relative permittivity was measured in the function of the field strength by means of a device similar to that of Małecki [10], which is a modified version of the apparatus developed by Kautzsch [6], Malasch [7], Gundermann [8], and Piekara [9]. Since the apparatus has been described in detail elsewhere [11], here the schematics of the device is shown as well as the measuring principle and only the most important characteristics are discussed.
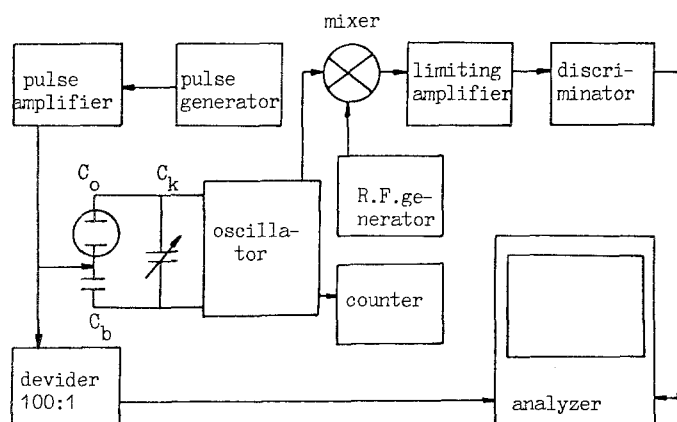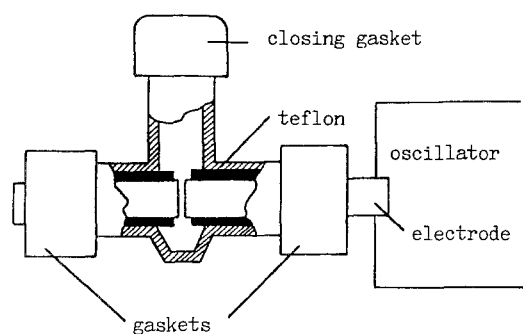
Fig. 1. The schematics of the apparatus

Fig. 2. The schematics of the measuring cell

The principle of Małecki's method — who modulated the radio-frequency electric field of the cell containing the liquid to be tested by high voltage pulses — was used. In that case the period of the modulating pulses was in the order of 1 ms. For such short time intervals (or less) the space between the electrodes can be considered as adiabatically isolated from its surroundings. This gives a possibility to separate the permittivity change caused by the change of the temperature ($\Delta \varepsilon_T$) from that caused by non-linear dielectric effect ($\Delta \varepsilon_E$). This principle was also applied by others [12–14] who tried to improve the method since Małecki used the FM-demodulating characteristic of a detuned oscillating circuit for the measurement of the frequency change during the pulse. We used a more sensitive method for the measurement. The schematics of the measuring device are shown in Figs. 1 and 2.

Some characteristic features of the most important units of the apparatus are listed below.

1. The individual pulses originate from a monostable multivibrator. The length of an impulse was varied in the 0.5 to 15 ms range.

2. The measuring cell was designed so that the significant forces developed during the pulses should not induce deformation (Fig. 2). The voltage gradient between the electrodes was about $10^6 \, V \, m^{-1}$. The cell — which contains stainless steel electrodes and teflon gaskets — can be thermostated. A Franklin 160 type LC oscillator was connected to the apparatus. Its frequency stability was about $10^{-3}\%$, the frequency could be varied in the 10 to 30 MHz range by the change of the inductivity.

3. After mixing, the difference frequency signal (10.7 MHz) was detached by a quartz filter. Since the amplitude of the oscillator signal also varies as a result of the high voltage pulse, a limiting amplifier tuned to 10.7 MHz was used before the demodulation.

4. A quartz discriminator was used for the demodulation of the FM-signal. Its signal — which is proportional to the frequency change — was displayed on an EMG TR-4910 type analyzer. The proper operation of the apparatus was checked by the measurement of the Piekara constants ($\lambda = \Delta\varepsilon/E^2$) of carbon tetrachloride and diethyl ether. The results showed a good agreement with literature data [11]. The accuracy of the measurement was found to be 5% and 8%, respectively. The apparatus is suitable for the investigation of liquids having specific conductances of less than $5\,\mu S\,cm^{-1}$.

Results

The experimental results are summarized in Tables 1, 2, and 3.

The excess volume of mixing is defined as usual by the following equations,

$$v^E = v - v^*,$$

where

$$v = \frac{x_1 M_1 + x_2 M_2}{\rho} \quad \text{and} \quad v^* = x_1 \frac{M_1}{\rho_1} + x_2 \frac{M_2}{\rho_2}.$$

In Table 3 y_1 is the molar fraction of cyclohexanone in the vapour phase, P is the total pressure, γ_1 and γ_2 are the activity coefficients of the components, while G^E is the excess Gibbs free energy of mixing. Considering the gas phase as an ideal one, the following equations were used for the calculations,

$$P y_i = P_i^0 x_i \gamma_i \qquad (i = 1, 2) \tag{1}$$

and

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2. \tag{2}$$

Table 1. Density (ρ) and the excess volume of mixing (v^E) of the cyclohexanone (1) + carbon tetrachloride (2) mixtures at 293.15 and 313.15 K

x_1	ρ (293.15) [kg m^{-3}]	ρ (313.15) [kg m^{-3}]	v^E(293.15) [cm^3 mol^{-1}]	v^E(313.15) [cm^3 mol^{-1}]
0.0000	1 513.16	1 554.46	—	—
0.1068	1 523.43	1 485.94	−0.248	−0.161
0.2045	1 459.45	1 424.70	−0.415	−0.360
0.3016	1 391.11	1 363.34	−0.502	−0.484
0.4036	1 328.98	1 298.78	−0.596	−0.547
0.4999	1 266.23	1 237.75	−0.618	−0.540
0.5994	1 201.33	1 175.00	−0.568	−0.496
0.6995	1 136.66	1 112.58	−0.477	−0.426
0.7988	1 073.32	1 051.19	−0.374	−0.326
0.8972	1 010.41	990.85	−0.159	−0.189
1.0000	946.48	928.40	—	—

Table 2. The static relative permittivity (ε), the *Piekara* constant (λ) as well as the refractive index (n_D) of the cyclohexanone (1) + carbon tetrachloride (2) mixtures at 313.15 K

x_1	n_D (313.15)	x_1	λ (313.15)	x_1	ε (313.15)
0.0000	1.4490	0.0000	1.4	0.0000	2.18
0.1108	1.4490	0.1031	−43.2	0.1023	3.05
0.1967	1.4490	0.1972	−117.0	0.2010	3.86
0.3006	1.4492	0.3010	−203.0	0.2972	4.75
0.3944	1.4495	0.3611	−267.0	0.4014	5.88
0.4975	1.4488	0.4109	−361.0	0.4955	7.09
0.5980	1.4480	0.5662	−573.0	0.5957	8.54
0.6997	1.4466	0.6018	−787.0	0.6987	10.13
0.7977	1.4453			0.7967	11.66
0.8955	1.4434			0.8840	12.99
1.0000	1.4419			1.0000	14.76

Table 3. Vapour-liquid equilibrium data of the cyclohexanone (1) + carbon tetrachloride (2) mixtures at 313.15 K

x_1	y_1	P [kPa]	$\ln \gamma_1$	$\ln \gamma_2$	G^E/RT
0.000	0.000	28.50	—	0.0000	0.000
0.108	0.007	25.92	0.1740	0.0125	0.030
0.148	0.010	24.99	0.1788	0.0185	0.040
0.276	0.021	21.99	0.1697	0.0423	0.077
0.388	0.033	19.32	0.1518	0.0688	0.101
0.492	0.046	16.72	0.1015	0.0965	0.099
0.588	0.064	14.21	0.0911	0.1245	0.105
0.676	0.086	11.74	0.0564	0.1504	0.089
0.800	0.144	8.09	0.0305	0.1942	0.063
0.840	0.178	6.83	0.0246	0.2078	0.054
0.904	0.273	4.74	0.0128	0.2297	0.034
1.000	1.000	1.41	0.0000	—	0.000

Discussion

The model used for the evaluation of the experimental data of the cyclohexanone + carbon tetrachloride mixtures has already been used successfully for the interpretation of the properties of mixtures consisting of a ketone + a nonpolar component [15–19]. Thus, three real components can be distinguished in the mixture: the keto-form (K), the keto-enol association (KE), and the carbon tetrachloride (B) component. The enol formation can be definied by the equilibrium of the following reaction,

$$2\,K \rightleftharpoons KE.$$
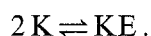
It means that the free enol which can possibly be present in the mixture in a very small amount is neglected. Under these conditions the thermodynamic equilibrium constant of the association reaction is as follows,

$$K = \frac{x_{KE}}{x_K^2} \cdot \frac{\gamma_{KE}}{\gamma_K^2} = K_x \cdot K_\gamma.$$ (3)

As for the interpretation of the dielectric properties it is supposed that the K_γ function which is determined by the activity coefficients is independent of the electric field strength, and it is a function of the temperature (and of course, the composition of the mixture), only,

$$K(T, \bar{E}) = K_x(T, \bar{E}) \cdot K_\gamma(T).$$ (4)

Under these conditions the equation introduced by Małecki [10] can be used. For the following type of reaction

$$m_1 A_1 + m_2 A_2 + \cdots \rightleftharpoons m_e A_e + m_{e+1} A_{e+1} + \cdots,$$ (5)
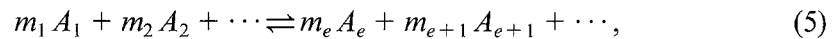
the correlation coefficients (R_p and R_s) can be given as follows,

$$R_p = \frac{1}{\bar{\mu}_1^2} \sum_i \frac{z_i}{i} \bar{\mu}_i^2,$$ (6)

$$R_s = \frac{1}{\bar{\mu}_1^4} \sum_i \frac{z_i}{i} \bar{\mu}_i^2 \left(\bar{\mu}_i^2 - \frac{5}{2} u_i \right)$$ (7)

where

$$z_i = \frac{i N_i}{\sum_i N_i} \quad \text{and} \quad u_i$$

are the solution of the following equation system,

$$\sum_i m_i u_i = \sum_i m_i \bar{\mu}_i^2,$$ (8)

$$\sum_i z_i u_i = 0.$$ (9)

Here $\bar{\mu}_i$ is the dipole moment of molecule i, while N_i is the number of molecules i.

As for the relationship between the correlation coefficients (R_s and R_p) and the dielectric properties (which can be measured directly), Małecki obtained the following equations on the basis of the macroscopic Onsager theory [20]:

$$R_p = \frac{27\varepsilon_0 kT [2\varepsilon(0) + n_2^2]^2}{N_0 \mu^2 x_1 [2\varepsilon(0) + 1](n_2^2 + 2)^2} \left\{ \frac{(M_1 x_1 + M_2 x_2)[\varepsilon(0) - 1]}{3\rho\varepsilon(0)} \right.$$
$$\left. - \frac{M_1 x_1 (n_1^2 - 1)}{\rho_1 [2\varepsilon(0) + n_1^2]} - \frac{M_2 x_2 (n_2^2 - 1)}{\rho_2 [2\varepsilon(0) + n_2^2]} \right\},$$ (10)

$$R_s = \frac{45\varepsilon_0 k^3 T^3 [2\varepsilon(0) + n^2]^2}{N_0 \mu^4 x_1 \varepsilon(0)^2 (n^2 + 2)^2} \left\{ \frac{[2\varepsilon(0) + n^4](M_1 x_1 + M_2 x_2)}{\varepsilon(0)^2 (n^2 + 2)^2 \rho} \cdot \lambda \right.$$
$$\left. - \frac{2\varepsilon(0)_2^2 + n_2^4 M_2 x_2}{\varepsilon(0)_2^2 (n_2^2 + 2)^2 \rho_2} \cdot \lambda_2 \right\},$$ (11)

where λ is the Piekara constant, ε_0 is the permittivity of vacuum, $\varepsilon(0)$ is the static relative permittivity measured in "0" electric field, M_1, M_2 are molar masses, k is the Boltzmann constant, N_0 is Avogadro's number, and n_1, n_2, n are refractive indices related to a light of infinite wavelength, replaced by values measured at the Na $-$ D line. The rest of the symbols were explained before.

Index 1 indicates the properties of the polar component (ketone), while index 2 belongs to the nonpolar component (carbon tetrachloride). Symbols without indices designate mixture properties.

The evaluation is carried out with the following assumptions:

(i) Suppose that Eqs. (10) and (11) (deduced by Małecki [20]) are valied for the mixture studied.

(ii) Eq. (4) is believed to be valid.

(iii) Since the relative enol content of the ketone extrapolated to an infinitely diluted mixture is not more than a few per cent even in nonpolar solvents, it is supposed that the dipole moment measured by May [21] using Deby's method can practically be considered as that of the keto-form, i.e. $\bar{\mu}_1 \approx \mu_K = 10.70 \cdot 10^{-30} \, C_m$ (3.12 D).

(iv) The refractive index related to a light of infinite wavelength can be replaced by the value measured at the Na $-$ D line.

If N_1 is the number of the ketone molecules (keto and enol forms together), N_K is the number of the keto-forms, and N_{KE} indicates the number of the keto-enol associations, then from Eqs. (10) and (11) it follows that

$$R_p = z_K + \frac{z_{KE} \, \bar{\mu}_{KE}^2}{2 \, \bar{\mu}_K^2}, \tag{12}$$

$$R_s = \frac{1}{\bar{\mu}_K^4} \left[z_K \, \bar{\mu}_K^2 \left(\bar{\mu}_K^2 - \frac{5}{2} u_1 \right) + \frac{z_{KE}}{2} \bar{\mu}_{KE}^2 \left(\mu_{KE}^2 - \frac{5}{2} u_2 \right) \right] . \tag{13}$$

On the basis of equation systems 8 and 9 determining u_1 and u_2 it can be written that

$$u_2 - 2 u_1 = \bar{\mu}_{KE} - 2 \bar{\mu}_K^2 \tag{14}$$

and

$$u_1 z_K + u_2 z_{KE} = 0, \tag{15}$$

where

$$z_K = \frac{N_K}{N_K + 2 N_{KE}} = \frac{N_K}{N_1}, \tag{16}$$

$$z_{KE} = \frac{2 N_{KE}}{N_K + 2 N_{KE}} = \frac{2 N_{KE}}{N_1}, \tag{17}$$

and it is true that

$$z_K + z_{KE} = 1. \tag{18}$$

Solving the equation system (14), substituting the values of u_1 and u_2 into Eq. (13), and using the simplifying suppositions listed above, Eqs. (12) and (13) contain two variables only, z_{KE} and μ_{KE}. The values of R_p and R_s are known from Eqs. (10) and (11) (from macroscopic measuring results).

Thus, expressing the two variables, the following equations can be obtained:

$$z_{KE}^3 + (4\,R_p - R_s - 2)\,z_{KE}^2$$
$$+ (7\,R_p^2 - R_s - 10\,R_p + 4)\,z_{KE} + 6\,R_p - 3\,R_p^2 - 3 = 0, \qquad (19)$$

$$\bar{\mu}_{KE} = \frac{2\,\mu_K^2\,(R_p - 1 + z_{KE})}{z_{KE}}. \qquad (20)$$

Thus, the dipole moment and the amount of the associations can be calculated from the measuring results using Eqs. (19) and (20).

The molar fractions (x_K, x_{KE}, x_B) in the ternary model of the true real components (K, KE, B) can be expressed by the following equations,

$$x_K = z_K \left(z_K + \frac{z_{KE}}{2} + \frac{1 - x_1}{x_1} \right)^{-1}, \qquad (21)$$

$$x_{KE} = \frac{z_{KE}}{2} \left(z_K + \frac{z_{KE}}{2} + \frac{1 - x_1}{x_1} \right)^{-1}. \qquad (22)$$

On the basis of Eqs. (21) and (22) the mass action fraction (K_x) can be expressed as follows,

$$K_x = \frac{z_{KE}}{2\,z_K^2} \left(z_K + \frac{z_{KE}}{2} + \frac{1 - x_1}{x_1} \right). \qquad (23)$$

The results calculated from the equations presented are considered as a first approach, since the dipole moment of the keto-form was estimated only. A more accurate calculation is possible if the enol content of the pure ketone is known and the $\bar{\mu}_{KE}$ data obtained for the dipole moment of the association in the first approach is used as well. Thus,

$$\bar{\mu}_1^2 \approx x_K^0\,\bar{\mu}_K^2 + x_{KE}^0\,\bar{\mu}_{KE}^2,$$

where index 0 designates the real mole fractions in the pure ketone. From this equation $\bar{\mu}_K$ can be estimated with the desired accuracy. After repeating the calculation, more accurate data can be obtained for x_{KE} and $\bar{\mu}_{KE}$. Calculating with $\bar{\mu}_K = 10.70 \cdot 10^{-30}\,\text{Cm}$ (3.12 D), the average dipole moment of the keto-enol association was found to be $1.18 \cdot 10^{-30}\,\text{Cm}$ (0.35 D). The calculated R_p and R_s coefficients, the mole fractions (x_{KE}) and the dipole moments ($\bar{\mu}_{KE}$) are shown in the function of the nominal ketone mole fraction in Figs. 3, 4, and 5.
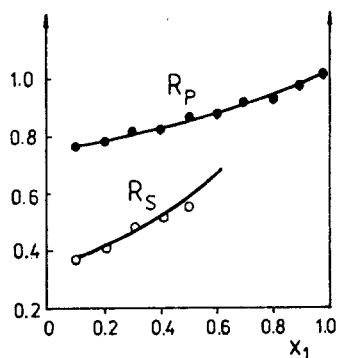

Fig. 3. The R_p and R_s correlation coefficients in the function of the nominal ketone molar fraction at 293.15 K
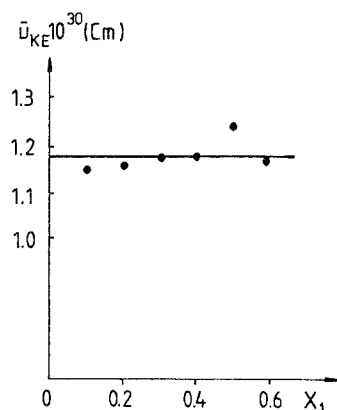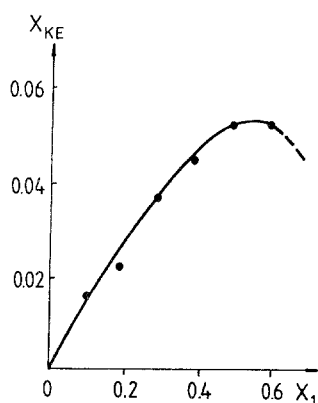
Fig. 4. Dipole moment of the KE association complex

Fig. 5. The molar fraction of the association at 293.15 K

On the basis of the results it can be seen that the dipole moment of the keto-enol association is very low, i.e. this association is almost nonpolar. Therefore, it is not surprising that in the nonpolar solvent (carbon tetrachloride) the equilibrium is shifted toward the formation of the association. Since $R_s > 0$, the saturation effect is normal. On the other hand, the correlation factor R_p decreases with the decreasing ketone mole fractions which means that the ketone becomes less polar at high dilution.

The dielectric results as well as the vapour-liquid equilibrium data of the nominal binary mixture allow the modelling of the excess Gibbs free energy of the system (G^E) in the form of an A, A_2, B-type real ternary mixture. In this case A = K (i.e. the keto-form), A_2 = KE (i.e. the association), and B is carbon tetrachloride.

The ternary mixture is in equilibrium at compositions determined by the association equilibrium constant, only. K_x changes with the composition so that the following equation is always fulfilled,

$$K = K_x K_\gamma = \text{constant.}$$

The activity coefficients were calculated in the function of the real composition using a modified form of the lattice model [22]. Thus, in the ternary mixture

$$\ln \gamma_i = \ln \gamma_i^* + \ln \gamma_i',$$

where the combinatorial contribution is calculated by the Flory approximation (φ_i is volume fraction),

$$\ln \gamma_i^* = \ln \frac{\varphi_i}{x_i} + 1 - \frac{\varphi_i}{x_i},$$

$$\ln \gamma_i' = q_i \{ \alpha_j^2 g(i,j) + \alpha_k^2 g(i,k) + [g(i,j) + g(i,k) - g(j,k)] \alpha_j \alpha_k \},$$

where

$$i = K, KE, B,$$
$$g(i,j) = g(j,i),$$
$$g(i,k) = g(k,i),$$
$$g(j,k) = g(k,j)$$

are the interaction parameters characteristic of the binary mixture, and α_i is the surface fraction of component i, which can be calculated by the following equation,

$$\alpha_i = \frac{x_i q_i}{\sum_i x_i q_i}.$$

The calculation of q_i was carried out on the basis of the molar volumes using the following approximation, or convention

$$q_K = 1,$$

$$q_{KE} = \left(\frac{v_{KE}}{v_K} \right)^{2/3} \approx \left(\frac{2 v_1^0}{v_1^0} \right)^{2/3} = 1.59,$$

$$q_B = \left(\frac{v_B}{v_K} \right)^{2/3} \approx \left(\frac{v_B^0}{v_1^0} \right)^{2/3}.$$

The four unknown parameters of the model [$g(K, KE)$; $g(K, B)$; $g(KE, B)$ and K] were fitted to the measured values of the $G^E/RT = f_1(x_1)$ and $\varepsilon^E = f_2(x_1)$ functions,

$$\varepsilon^E = \varepsilon_{measured} - \varepsilon^*,$$
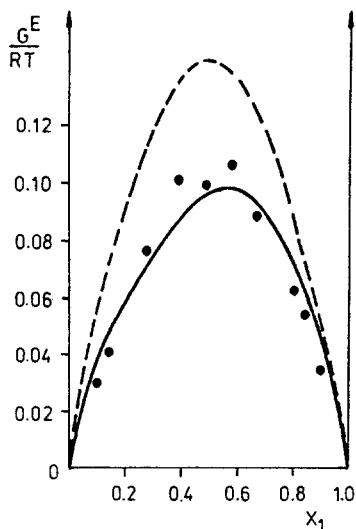

Fig. 6. The excess Gibbs free energy of the mixture in the function of the nominal ketone molar fraction at 313.15 K. Measuring results (●), according to the K + KE + B model (—), without association (— — —)
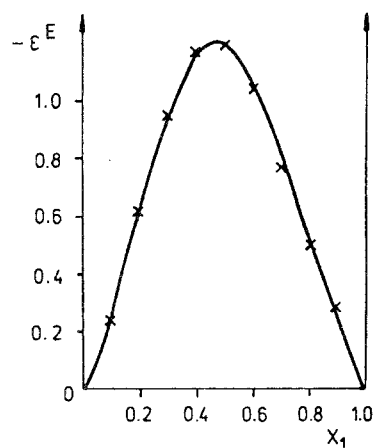
Fig. 7. The excess static relative permittivity of the mixture in the function of the nominal ketone molar fraction at 313.15 K
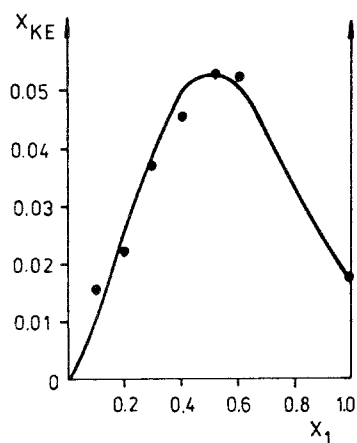

Fig. 8. The molar fraction of the KE association in the function of the nominal ketone molar fraction. Calculated from the ternary mixture model ($-$), determined by the dielectric method (●)

where ε^* is the probable static relative permittivity of the ideal mixture on condition that the Onsager equation is valid.

The measured and the calculated (by means of the ternary mixture model) results are shown in Figs. 6 and 7. The possible G^E/RT function of the ketone + carbon tetrachloride mixture without enol formation is also shown. It can be seen that the enol formation and the subsequent association significantly modify the G^E/RT function. The figures obtained for the parameters of the model are as follows,

$$g(K, B) = \quad 0.5649, \qquad K_x^0 = \quad 0.018, \qquad \varepsilon_1 = 14.76,$$
$$g(KE, B) = -1.020, \qquad v_1 = 105.72, \qquad \varepsilon_2 = \quad 2.18.$$
$$g(K, KE) = \quad 1.4404, \qquad v_2 = 100.24,$$
$$K_0 = \quad 0.1225, \qquad n_1 = \quad 1.4419,$$
$$x_{KE}^0 = \quad 0.0175, \qquad n_2 = \quad 1.4490,$$

The x_{KE} molar fraction calculated from the ternary mixture model as well as the experimental data obtained by the dielectric method are shown in Fig. 8.

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