

Role of Associated Complex in Determining the Magnitude of Excess Volumes of Binary Liquid Mixtures: Part I—Aniline & Methyl-substituted Anilines with Cyclohexane as Inert Diluent

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Excess volumes of binary mixtures of cyclohexane with *o*-toluidine, *m*-toluidine, N-methylaniline, and N,N-dimethylaniline have been presented as a function of composition. The magnitudes of excess volumes of the binary systems are discussed in terms of molecular interactions.

ANILINE and substituted anilines are associated in the pure state through hydrogen bonding and electron donor-acceptor interactions^{1,2}. If a non-associated inert diluent like cyclohexane is added to anilines, breaking up of the associated molecules may occur. Consequently, the excess volumes (V^E) will be positive and would generally show the maximum of excess volume in the lower composition of the associated liquid in the mixtures. The difference in the values of V^E may be used as a guide to the extent of self-association of the anilines. The results of such a study are presented in this paper.

Materials and Methods

The reagents used were of BDH quality and purified further employing the standard methods described earlier³. The purity of the samples has been ascertained through their density values which agree with the reported values within two in 10⁴.

The excess volumes have been computed from the density (determined by pycnometric method)

and the compositions of the mixtures, prepared in airtight conical flasks, as described earlier³.

Results and Discussion

The excess volumes of the binary mixtures of cyclohexane with *o*-toluidine, *m*-toluidine, N-methylaniline, and N,N-dimethylaniline at 303.15K are given in Table 1. The composition is expressed in terms of the mole fraction x_1 of aniline.

The results are fitted, by the least squares method, to the expression:

$$V^E(\text{cm}^3 \text{ mole}^{-1}) = x_1(1-x_1)[A+B(1-2x_1) + C(1-2x_1)^2] \dots (1)$$

in which x_1 is the mole fraction of aniline. The coefficients A , B and C are given in Table 2 together with the standard deviations σV^E of the excess volumes.

For all the mixtures, V^E is positive with its maximum lying in the lower percentage of aniline, showing that anilines are associated in the pure state.

TABLE 1 — EXPERIMENTAL VALUES OF V^E FOR MIXTURES OF SOME ANILINES WITH CYCLOHEXANE AT 303.15K

(x ₁ is the mole fraction of the aniline)									
<i>o</i> -TOLUIDINE + CYCLOHEXANE									
x ₁	0.1004	0.2019	0.3080	0.4129	0.4991	0.5973	0.6992	0.7974	0.8997
V ^E (cm ³ mole ⁻¹)	0.36	0.49	0.53	0.52	0.47	0.41	0.30	0.20	0.11
<i>m</i> -TOLUIDINE + CYCLOHEXANE									
x ₁	0.1000	0.2019	0.3001	0.4016	0.5003	0.5998	0.6980	0.8002	0.9012
V ^E (cm ³ mole ⁻¹)	0.39	0.50	0.53	0.51	0.46	0.40	0.32	0.23	0.13
N-METHYLANILINE + CYCLOHEXANE									
x ₁	0.1032	0.2021	0.3009	0.4019	0.4984	0.5968	0.7000	0.8000	0.9020
V ^E (cm ³ mole ⁻¹)	0.32	0.42	0.45	0.46	0.42	0.32	0.26	0.16	0.09
N,N-DIMETHYLANILINE + CYCLOHEXANE									
x ₁	0.1010	0.1998	0.3008	0.4004	0.5006	0.6002	0.7002	0.8027	0.9006
V ^E (cm ³ mole ⁻¹)	0.32	0.51	0.57	0.58	0.51	0.41	0.34	0.23	0.15

TABLE 2—VALUES OF THE COEFFICIENTS IN EQ. (1)

(Temp. = 303.15 K)

Binary mixture of cyclo- hexane with	A	B	C	σV^E (cm^3 mole^{-1}) (SD)
<i>o</i> -Toluidine	1.8424	-1.6035	1.0991	0.009
<i>m</i> -Toluidine	1.7887	-1.5862	1.6349	0.024
N-Methylaniline	1.5680	-1.4242	0.9573	0.019
N,N-Dimethyl- aniline	2.0259	-1.2934	0.8815	0.915

Since cyclohexane+aniline system has a critical solution temperature of 304.65K (ref. 4), it was not possible to study the system at 303.15K. Hence the excess volume at equimolar composition of cyclohexane+aniline system, 0.37 $\text{cm}^3 \text{mole}^{-1}$ reported by Wellm⁵ at 305.15K has been used for comparison purposes. The experimental V^E values of the mixtures of anilines with cyclohexane at equimolar compositions are in the order: aniline < N-methylaniline < *o*-toluidine \approx *m*-toluidine < N,N-dimethylaniline (Table 1). The H^E values reported by Sosnkowska-kehiaian *et al.*⁶ for the mixtures of aniline, N-methylaniline and N,N-dimethylaniline with cyclohexane at 323.15K are in the order: aniline (2092 $J \text{mole}^{-1}$) > N-methylaniline (1778 $J \text{mole}^{-1}$) > N,N-dimethylaniline (1151 $J \text{mole}^{-1}$). These results show that the volume change depends on the extent of dissociation of the associated molecules and the enthalpy change on the energy of dissociation of the more local bonds which lead to the association (whether hydrogen bond or $n-\pi$ or $\pi-\pi$).

The introduction of a methyl group, both in the benzene ring and at the nitrogen atom of the amino group, would increase the electron density of amino nitrogen by inductive effect. Hence, the hydrogen atoms of the amino group in toluidines and N-methylaniline would be held more firmly to nitrogen than in aniline. On the other hand, due to the

increased electron density around nitrogen, the tendency of the lone pair of electrons on the nitrogen to attract labile hydrogen from other molecule would also increase. The degree of association in the pure state of toluidines and N-methylaniline as compared to aniline would, therefore, depend on which of the two factors dominates. The nearly equal values of V^E for the mixtures of *o*-toluidine and *m*-toluidine with cyclohexane, where the pK_a values⁷ of the two anilines are respectively 4.5 and 4.8 as well as the different values of V^E of the mixtures of *m*-toluidine and N-methylaniline with cyclohexane, where the pK_a values⁷ of the bases are equal (4.8) indicate that enhancement of electron density at nitrogen atom due to the methyl substituent favours both the opposing effects described above equally. The difference in the magnitudes of V^E values may be attributed to steric effects. The smaller V^E values of N-methylaniline+cyclohexane system compared to the toluidines+cyclohexane systems show that the methyl group in the ring contributes to a greater extent to the weakening of the association. It would also indicate that the $\pi-\pi$ interactions here are as important as the hydrogen bond interactions, since the ring methyl group can cause no steric effect on the hydrogen bond formation involving the amino groups.

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