

Notes

Significance of the Newly Proposed Equation for the Determination of Dipole Moment in Solution

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A critical examination of the newly proposed equation¹ when applied to the experimental data reported earlier^{2,3} reveals that the equation¹ is less accurate than most of the equations available in the literature^{4,5}. The method and technique used by us have been discussed elsewhere^{2,3}.

From the worked out data¹ and the data shown here in the table 1, it can be easily concluded that the agreement shown by the authors¹ in certain cases

appears to be fortuitous. Further in the name of fair agreement an error nearly of 8% in case of Bromobenzene is questionable. However it is pertinent to point out that the error between the calculated and the experimental values seems to be a function of the dielectric constant of the solute or the factor $\epsilon_2^{+2}/\epsilon_1^{+2}$. This is further substantiated when the case of Nitrobenzene in cyclohexane is considered (Table 1). In this particular case the two values i.e., the one calculated by the newly proposed equation¹ and the other available in the literature, are widely divergent. Consequently such data with this discrepancy for the purpose of interpreting the results is but to lead to a doubtful conclusion.

The inclusion of chlorobenzene by the authors¹ in the list of those involving no specific interaction is a point of discussion. In earlier papers³ we have already shown the importance of the Eap and Glasstone theory⁶ to study the specific interaction in solution. Accordingly the excess polarisation P^E

TABLE 1
In Benzene

S.No.	Name of the compound	By New Empirical eq.		By Halverstadt Kumler eq.		Literature value	$\frac{\epsilon_2^{+2}}{\epsilon_1^{+2}}$
		$P_2\infty$	μ	$P_2\infty$	μ		
1.	Chlorobenzene	92.54	1.76	81.63	1.60	1.60	1.82
2.	Bromobenzene	90.76	1.68	89.20	1.66	1.54	1.75
3.	Nitrobenzene	613.18	5.37	372.40	4.11	4.11	8.62
4.	Pyridine	150.13	2.52	131.54	2.33	2.28	3.28
5.	n-Amylamine	84.19	1.66	72.54	1.47	1.55	1.55
6.	Di-n-amylamine	82.66	1.23	76.58	1.11	—	1.12
7.	n-Propylmercaptan	77.96	1.64	72.24	1.55	1.51	1.78
8.	n-Butylmercaptan	86.54	1.70	78.46	1.58	1.53	1.66
9.	Iso-butylmercaptan	84.98	1.68	74.14	1.51	1.53	1.63
10.	Benzyl-mercaptan	129.38	2.12	77.26	1.38	—	1.57
In Cyclohexane							
1.	Chlorobenzene	96.08	1.80	93.35	1.76	—	1.93
2.	Bromobenzene	94.33	1.73	91.16	1.69	1.57	1.86
3.	Nitrobenzene	644.41	5.39	384.92	4.19	4.12	9.18
4.	Pyridine	156.06	2.58	135.46	2.37	2.28	3.49
5.	n-Propylmercaptan	80.55	1.68	98.15	1.92	—	1.90
6.	n-Butylmercaptan	90.30	1.75	79.42	1.59	—	1.78
7.	Iso-butylmercaptan	88.35	1.72	68.88	1.42	—	1.74

(Table 2) for the system (chlorobenzene + benzene) is a linear function of $f_1 f_2$ and passes through the origin. This suggests that the charge transfer type complexes are formed between chlorobenzene and benzene.

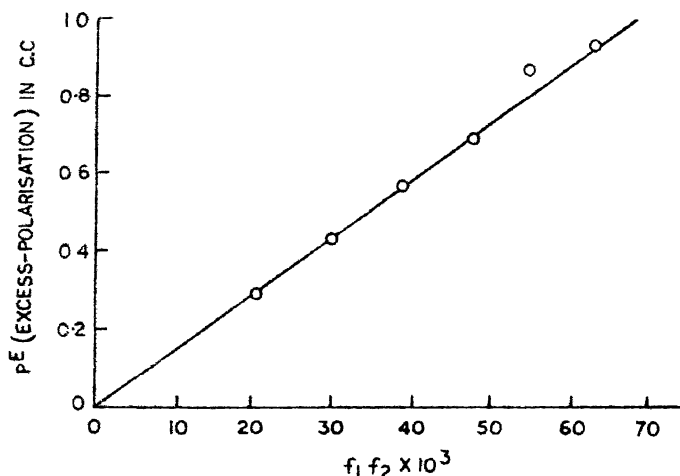


Fig. 1. Chlorobenzene in benzene.

It is worth mentioning here that for practical purposes a careful application of the equations¹ is desirable.

TABLE 2—CHLOROBENZENE IN BENZENE

(1)	(2)	(3)	(4)
$f_1 f_2$	Solution Polarisation P_{12}	Total Polarisation of the solution $P_{12} =$ $P_1 F_1 + P_2 F_2$	Excess Polarisation PE (2) - (3)
0.0204	27.687	27.394	+0.293
0.0300	28.191	27.764	+0.427
0.0390	28.663	28.113	+0.550
0.0481	29.167	28.479	+0.688
0.0552	29.635	28.765	+0.870
0.0633	30.029	29.104	+0.925

ϵ_1 (dielectric constant of solvent)	= 2.2617
ϵ_2 (dielectric constant of solute)	= 5.7407
d_1 (density of solvent)	= 0.8679 g/ml.
d_2 (density of solute)	= 1.0955 g/ml.

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Transport Processes and Some New Symmetries

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IN continuation to our earlier communication¹, we now report on the occurrence of some new symmetries, about which only a scanty information is available in the literature^{2,3} and that too without any systematic elaboration.

If J'_1, J'_2, \dots, J'_r be the independent linear combinations of some original flows J_1, J_2, \dots, J_r each of which is represented as

$$J_i = \left(\frac{\partial J_i}{\partial X_i} \right)_0 X_i + \frac{1}{2!} \left(\frac{\partial^2 J_i}{\partial X_i^2} \right)_0 X_i^2 + \frac{1}{3!} \left(\frac{\partial^3 J_i}{\partial X_i^3} \right)_0 X_i^3 + \dots \quad (i = 1, 2, \dots, r) \quad \dots (1)$$

and likewise their corresponding conjugate forces X'_1, X'_2, \dots, X'_r be the linear combinations of the original forces X_1, X_2, \dots, X_r as given under

$$\begin{bmatrix} J'_1 \\ J'_2 \\ \vdots \\ J'_r \end{bmatrix} = \begin{bmatrix} n_{11} & n_{12} & \dots & n_{1r} \\ n_{21} & n_{22} & \dots & n_{2r} \\ \dots & \dots & \dots & \dots \\ n_{r1} & n_{r2} & \dots & n_{rr} \end{bmatrix} \begin{bmatrix} J_1 \\ J_2 \\ \dots \\ J_r \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} X'_1 \\ X'_2 \\ \dots \\ X'_r \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & \dots & a_{1r} \\ a_{21} & a_{22} & \dots & a_{2r} \\ \dots & \dots & \dots & \dots \\ a_{r1} & a_{r2} & \dots & a_{rr} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ \dots \\ X_r \end{bmatrix} \quad \dots (2)$$

the n th order coefficient^{1,4,5} L_n is obtained as

$$L_n = \left(\begin{matrix} n_1 & n_2 & \dots & n_r \\ n_{11} & n_{21} & \dots & n_{r1} \end{matrix} \right) \left(\frac{\partial^n J_1}{\partial X_1^n} \right)_0 + \left(\begin{matrix} n_1 & n_2 & \dots & n_r \\ n_{12} & n_{22} & \dots & n_{r2} \end{matrix} \right) \left(\frac{\partial^n J_2}{\partial X_2^n} \right)_0 + \dots + \left(\begin{matrix} n_1 & n_2 & \dots & n_r \\ n_{1r} & n_{2r} & \dots & n_{rr} \end{matrix} \right) \left(\frac{\partial^n J_r}{\partial X_r^n} \right)_0 \quad \dots (3)$$

where $\sum_{k=1}^r n_k = n+1$.

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