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EXCESS VISCOSITIES OF BINARY MIXTURES OF γ-BUTYROLACTONE WITH ISOALCOHOLS

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Densities and viscosities of binary liquid mixtures of γ-butyrolactone as common component with isopropanol, isobutanol and isopentanol as non-common components were determined over the entire mole fraction range at 303.15 K. The values of η^E are negative over the entire composition range. Further, the study has been extended to evaluate interaction parameter, *d*. The values of both η^E and *d* indicate the existence of dispersion forces between unlike molecules; intermolecular interactions between unlike molecules are explained in terms of excess Gibbs free energy for activation of flow (G^E), and interaction energy (W_{visc}).

INTRODUCTION

The present work forms of a programme of measurement of viscosities of binary solutions of non-electrolytes. Viscosity data of binary liquid mixtures have been extensively employed to yield information regarding the nature of interactions in solutions,[1-9] the present paper includes the excess viscosities (η^E) of the systems γ-butyrolactone with isopropanol, isobutanol and isopentanol. The viscosity results have been discussed in the light of the viscosity-composition relations developed by Grunberg and Nissan[10] and Katti and Chaudhari[11] for non-ideal solutions and to evaluate strength of interaction parameter (*d*), interaction energy (W_{visc}) and excess free energy for activation of flow (G^E).

EXPERIMENTAL

Isoalcohols were purified by the methods described by Riddick and Bunger[12]. γ-Butyrolactone (Koch-light, England) was distilled and fractionated. The purity of the samples was checked by comparing the measured densities of the samples with those reported in the literature[13].

Viscosities of liquids and liquid mixtures were determined using Ostwald viscometer. The accuracy of the viscometer was checked by measuring the viscosities of pure benzene and cyclohexane. The results show good agreement with those reported in the literature[13]. Mixtures of various known compositions were prepared by weight. A constant volume of mixture was transferred into the viscometer and then inserted in a water thermostat controlled at 303.15 ± 0.01 K. The time of flow of the liquid through capillary was determined. Viscosity (η_m) was then obtained from density (ρ), flow time (t) and constant of the viscometer (K_v) using the relation

$$\eta_m = K_v \rho t. \tag{1}$$

Densities of pure components were determined experimentally. In case of mixtures densities were computed from excess volumes reported elsewhere[14] using the relation

$$\rho = \frac{XM_1 + (1-x)M_2}{V^o + V^E} \tag{2}$$

where x stands for molefraction of γ-butyrolactone. M_1 and M_2 are molecular weights of components 1 and 2 respectively, V^o and V^E denote the ideal molar volume and excess molar volume respectively.

Theoretical Aspects

Excess viscosity (η^E) at each composition is obtained from the relation suggested by Fort and Moore[5]

$$\eta^E = \eta_m - [X\eta_1 + (1-x)\eta_2] \tag{3}$$

where η_m is the viscosity of the mixture, η_1 and η_2 are the viscosities of γ-butyrolactone and non-common component respectively.

Excess Gibbs free energy for activation of flow (G^E) was calculated using Eyring's relation[15]

$$G^E = RT\,[\ln \eta V - X \ln \eta_1 V_1 - (1-x) \ln \eta_2 V_2] \tag{4}$$

Grunberg and Nissan[10] formulated the following expression to define the interaction parameter, d.

$$d = \frac{1}{X(1-x)}\,[\ln \eta - X \ln \eta_1 - (1-x) \ln \eta_2] \tag{5}$$

Katti and Chaudhari[11] deduced the following expression to show the variation of viscosity with molar volume and composition.

$$W_{\text{visc}} = \frac{RT}{X(1-x)}\,[\ln \eta V - x \ln \eta_1 V_1 - (1-x) \ln \eta_2 V_2] \tag{6}$$

where W_{visc} represents the interaction energy between the components.

RESULTS AND DISCUSSION

Excess viscosities of mixtures of γ-butyrolactone with isoalcohols are given in Table 1. The dependence of η^E on molefraction is expressed by an empirical equation of the form

$$\eta^E = X_1X_2\,[C_0 + C_1(X_1 - X_2) + C_2(X_1 - X_2)^2] \tag{7}$$

where C_0, C_1 and C_2 are the adjustable parameters on computing by the method of least squares. The values of parameters C_0, C_1 and C_2 along with standard deviation (η^E) are given in Table 2. η^E was computed employing the relation

TABLE 1

MOLE FRACTIONS (x_1) OF γ-BUTYROLACTONE, VISCOSITY OF THE MIXURE, (η_{mix}), EXCESS VISCOSITIES (η^E), log OF KINEMATIC VISCOSITY ($\ln \eta V$), STRENGTH OF INTERACTION PARAMETER (d), INTERACTION ENERGY (W_{vics}), EXCESS GIBBS FREE ENERGY FOR ACTIVATION OF FLOW (G^E) FOR THE MIXTURES OF γ-BUTYROLACTONE WITH ISOALCOLS AT 303.15 K

x_1	ρ	η_{mix}	η^E	$\ln \eta V$	d	W_{visc}	G^E
	g cm^{-3}	cP	cP			cal mol^{-1}	cal mol^{-1}
γ–Butyrolactone + isopropanol							
0.0000	0.77691	1.768	—	4.918	—	—	—
0.1304	0.82205	1.429	–0.314	4.705	–1.744	–1050.340	–119.109
0.2194	0.85284	1.313	–0.412	4.620	–1.588	–956.894	–163.878
0.3228	0.88847	1.250	–0.455	4.570	–1.414	–852.055	–186.259
0.4616	0.93603	1.228	–0.450	4.552	–1.251	–753.380	–187.237
0.5845	0.97774	1.229	–0.426	4.552	–1.218	–733.516	–178.142
0.6736	1.00781	1.241	–0.396	4.562	–1.254	–755.252	–166.050
0.8183	1.05635	1.304	–0.305	4.611	–1.408	–847.987	–126.087
0.9176	1.08962	1.414	–0.176	4.691	–1.544	–930.394	–703.347
1.0000	1.11730	1.574	—	4.798	—	—	—
γ–Butyrolactone + isobutanol							
0.0000	0.79439	2.873	—	5.591	—	—	—
0.1404	0.83326	1.987	–0.704	5.198	–2.355	–1408.272	–169.964
0.2443	0.86320	1.698	–0.858	5.022	–2.052	–1226.773	–226.487
0.3724	0.90162	1.562	–0.827	4.915	–1.649	–982.288	–229.580
0.5071	0.94378	1.518	–0.696	4.861	–1.332	–791.129	–197.743
0.6153	0.97921	1.489	–0.585	4.821	–1.212	–719.234	–170.250
0.7172	1.01232	1.452	–0.495	4.776	–1.238	–734.661	–150.429
0.7940	1.04083	1.429	–0.413	4.744	–1.349	–801.072	–131.023
0.9044	1.08100	1.446	–0.252	4.733	–1.646	–980.186	–84.747
1.0000	1.11730	1.574	—	4.798	—	—	—
γ–Butyrolactone + isopentanol							
0.0000	0.80177	2.962	—	5.786	—	—	—
0.2122	0.85247	2.059	–0.608	5.357	–1.373	–791.485	–132.313
0.3398	0.88628	1.821	–0.669	5.192	–1.211	–692.943	–155.455
0.3711	0.89500	1.775	–0.672	5.156	–1.189	–679.389	–158.556
0.4066	0.90510	1.733	–0.665	5.120	–1.156	–659.393	–159.098
0.5954	0.96300	1.568	–0.568	4.954	–1.078	–610.507	–147.071
0.7642	1.02156	1.473	–0.428	4.828	–1.195	–679.705	–122.483
0.8396	1.05025	1.461	–0.336	4.790	–1.306	–745.709	–100.425
0.9156	1.08089	1.486	–0.205	4.776	–1.435	–822.419	–63.557
1.0000	1.11730	1.574	—	4.798	—	—	—

TABLE 2
VALUES OF THE PARAMETERS C_0, C_1 AND C_2 OF THE EQUATION (7) AND THE STANDARD DEVIATION $\sigma(\eta^E)$ AT 303.15K

γ-Butyrolactone +	C_0	C_1	C_2	$\sigma(\eta^E)$
Isopropanol	−1.782	0.397	−1.267	0.001
Isobutanol	−2.814	2.154	−2.826	0.002
Isopentanol	−1.523	1.068	−2.504	0.003

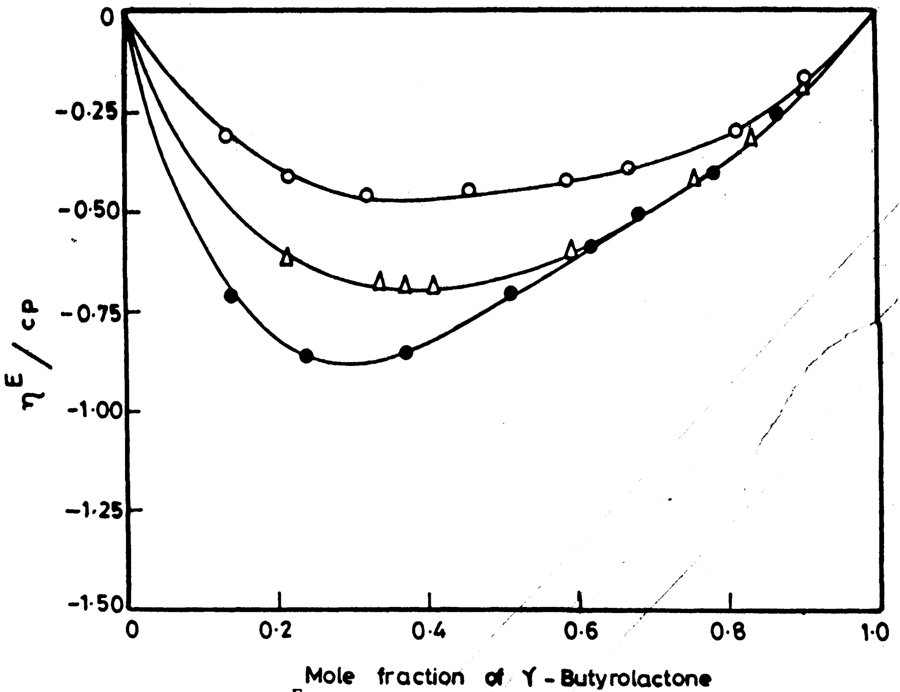

Fig. 1 Excess Viscosities (η^E) for γ-Butyrolactone + Propan-ol-2-ol(O), 2 Methylpropane-1-ol (●) and +3 Methylbutan-1-ol (Δ) at 303.15K.

$$\sigma(\eta^E) = \left[\frac{\Sigma[\eta^E_{(\text{expt})} - \eta^E_{(\text{eq.7})}]^2}{(\eta - \rho)}\right]^{1/2} \tag{8}$$

where η and ρ stand for number of results and number of parameters respectively used in the equation 7. The excess viscosity composition plots of these mixtures graphically presented in Fig. 1 indicate that E exhibits negative deviation over entire range of mole fraction. The values of density (ρ), viscosity (η), excess viscosity (η^E), log g, kinematic viscosity (ln ηV), excess free energy for activation of flow (G^E), interaction energy (W_{visc}) and parameter d are also given in Table 1. The data show that the values of η^E are negative over the entire range of composition for all the systems. In systems where all types of interactions are operating, the values of η^E will be determined by the predominant effect. Negative η^E values in systems of γ-butyrolactone with isoalcohols fall in the order:

isobutanol > isopentanol > isopropanol

This order indicates that increase in branching of alcohol results in decrease of hydrogen bonding between alcohol and lactone, which may be attributed to steric effect. The negative η^E values may be attributed to the (i) difference in size and shape of the component molecules, loss of dipolar association of γ-butyrolactone molecules on the addition of alcohols and depolymerisation of alcohols on the addition of lactone (ii) and specific interaction between unlike molecules. The data included in Table 1 indicate that the former effect contributes to viscosity over the entire composition range in the mixtures of γ-butyrolactone with isoalcohols.

An examination of d and W_{visc} values in Table 1 reveals that the values of W_{visc} almost unparallel with d in all the systems. The variations of d and W_{visc} with composition are considerable. The negative values of d indicate very weak interaction between unlike molecules. The values of excess Gibbs free energy for activation of flow (G^E) included in Table 1 suggest that the behaviour of the systems is in line with the observations made by Reed and Taylor[16].

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